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LXXVI.—ON CHLORSULPHOPYROMUCIC ACIDS.[1]

BY HENRY B. HILL AND WALTER S. HENDRIXSON.

The sulphonic acids which may be formed by the action of fuming sulphuric acids upon the several brompyromucic acids were described a few years ago by Hill and Palmer.[2] The chlorpyromucic acids, which were at that time unknown, were afterwards studied by Hill and Jackson,[3] and were shown to differ in certain respects quite essentially from the corresponding bromine derivatives. It therefore seemed to us advisable to study also the behavior of these acids toward fuming sulphuric acid.

β-CHLOR-δ-SULPHOPYROMUCIC ACID.

β-chlorpyromucic acid dissolves readily in fuming sulphuric acid (sp. gr. 1.95), and the corresponding sulphonic acid is rapidly formed without appreciable carbonisation. The β-chlorpyromucic acid itself we prepared by reducing βγ-dichlorpyromucic acid with sodium amalgam containing one per cent. of sodium. Complete reduction could be effected by using one and a half times the calculated amount of amalgam, and about fifty per cent. of the theoretical yield of β-chlorpyromucic acid was obtained. The β-chlor-δ-sulphopyromucic acid was isolated in the usual way,

[1] Presented at a meeting of the American Academy of Arts and Sciences, held February 11, 1891.

[2] This Journal **10**, 373 and 409; and Proc. Am. Acad. **23**, 188.

[3] This Journal **12**, 22 and 112; and Proc. Am. Acad. **24**, 320.

after neutralising the diluted acid solution with baric carbonate. The free acid crystallises in hemispherical masses of indistinct radiating needles, which deliquesce rapidly when exposed to moist air.

Baric β-Chlor-δ-Sulphopyromucate, $BaC_5HClSO_6.4H_2O$.

This salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallises in prisms which contain four molecules of water. When exposed to the air it slowly effloresces, and loses its water readily over sulphuric acid or when heated to 100°.

I. 0.7880 gram of salt dried by short exposure to the air gave 0.4246 gram $BaSO_4$.

II. 0.6729 gram air-dried salt gave 0.3631 gram $BaSO_4$.

III. 1.5568 grams air-dried salt lost at 100° 0.2547 gram H_2O.

IV. 1.1932 grams air-dried salt lost over H_2SO_4 0.1935 gram H_2O.

	Calculated for $BaC_5HClSO_6.4H_2O$.	Found. I.	II.	III.	IV.
Ba	31.60	31.63	31.72	...	...
H_2O	16.61	...	...	16.36	16.22

I. 0.6958 gram salt dried at 100° gave 0.4477 gram $BaSO_4$.

II. 1.0371 grams salt dried over H_2SO_4 gave 0.6678 gram $BaSO_4$.

	Calculated for BaC_5HClSO_6.	Found. I.	II.
Ba	37.89	37.83	37.86

The solubility of the salt in cold water we determined in the usual way.

I. 15.6246 grams solution saturated at 20° gave 0.1888 gram $BaSO_4$.

II. 17.2519 grams solution saturated at 20° gave 0.2084 gram $BaSO_4$.

The solution saturated at 20° therefore contained the following percentages of anhydrous salts:

I.	II.
1.87	1.87

Plumbic β-Chlor-δ-Sulphopyromucate, $PbC_5HClSO_6.4H_2O$.

The lead salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallises when its hot aqueous solu-

tion is cooled in thick rhombic prisms which contain four molecules of water. The salt effloresces slowly when exposed to the air, loses the greater part of its water over sulphuric acid, and becomes anhydrous when heated to 125°.

I. 0.7342 gram air-dried salt gave 0.4416 gram $PbSO_4$.

II. 1.7839 grams air-dried salt lost at 125° 0.2552 gram H_2O.

III. 0.7343 gram air-dried salt lost at 125° 0.1045 gram H_2O.

	Calculated for $PbC_5HClSO_6.4H_2O$.	Found. I.	II.	III.
Pb	41.11	41.09	...	...
H_2O	14.30	...	14.31	14.23

I. 0.6298 gram salt dried at 125° gave 0.4416 gram $PbSO_4$.

II. 0.6611 gram salt dried at 125° gave 0.4634 gram $PbSO_4$.

	Calculated for PbC_5HClSO_6.	Found. I.	II.
Pb	47.97	47.88	47.88

Potassic β-Chlor-δ-Sulphopyromucate, $K_2C_5HClSO_6.H_2O$.

The potassium salt was readily soluble even in cold water, but was obtained by cooling a hot concentrated aqueous solution in the form of transparent prisms, which effloresced over sulphuric acid.

I. 0.7895 gram air-dried salt gave 0.4260 gram K_2SO_4.

II. 1.7840 grams air-dried salt lost at 110° 0.1104 gram H_2O.

	Calculated for $K_2C_5HClSO_6.H_2O$.	Found. I.	II.
K	24.39	24.22	...
H_2O	5.61	...	6.18

I. 0.9626 gram salt dried at 110° gave 0.5464 gram K_2SO_4.

II. 0.7043 gram salt dried at 110° gave 0.4003 gram K_2SO_4.

	Calculated for $K_2C_5HClSO_6$.	Found. I.	II.
K	25.83	25.48	25.52

While there could be little doubt of the constitution of the sulphonic acid formed from β-chlorpyromucic acid, we attempted to establish more definitely the position of its sulpho-group by reducing it to the δ-sulphopyromucic acid. We found, however, that the chlorine was much more firmly held than the bromine of the corresponding β-brom-δ-sulphopyromucic acid, and that the reduction could not be effected by the ordinary reducing agents.

Zinc dust in an ammoniacal solution, which had given satisfactory results with the bromsulphopyromucic acids, removed the chlorine so slowly that, even after boiling the solution for days, the reduction was far from complete. On the other hand, sodium amalgam added to the aqueous solution of the barium salt at once attacked the sulpho-group, baric sulphite was precipitated, and β-chlorpyromucic acid was formed. With other reducing agents in acid solution we were equally unsuccessful. The ready elimination of the sulpho-group by the action of sodium amalgam in alkaline solution was so unexpected that we were led to examine the behavior of other sulphopyromucic acids under the same conditions. We found that δ-sulphopyromucic acid was thus readily reduced to pyromucic acid, while β-sulphopyromucic acid was apparently unaffected, and that the halogen derivatives of these two acids which we had at our disposal showed precisely the same difference in behavior. The removal of the sulpho-group from the chlorsulphopyromucic acid in question may therefore be taken as evidence that the sulpho-group is in the δ-position.

Action of Bromine.

Like all the derivatives of δ-sulphopyromucic acid which have thus far been examined, β-chlor-δ sulphopyromucic acid is at once oxidised by bromine in aqueous solution, and sulphuric acid is formed. Bromine was added in slight excess to a solution of the barium salt of the acid, the baric sulphate removed by filtration, and the acid filtrate extracted with ether. The acid thus obtained was very readily soluble in water and practically insoluble in benzol. After recrystallisation from water it was dried and washed with benzol. The acid thus purified melted at 188°, and with the quantity at our command we found it impossible to raise this melting-point. Although chlorfumaric acid melts at 191°,[1] there can be no doubt that chlorfumaric acid had been formed in the reaction.

Action of Nitric Acid.

Like the brom-δ-sulphopyromucic acids, the β-chlor-δ-sulphopyromucic acid is readily converted into the corresponding nitro-acid by the action of fuming nitric acid. For its preparation we dissolved the dry sulphonic acid in cold fuming nitric acid, warmed

[1] Kauder: J. prakt. Chem. [2] **31**, 28.

the solution for some time upon the water-bath, and finally evaporated the nitric acid at a gentle heat. The crystalline product thus obtained was recrystallised first from water, then from benzol, and finally from water. The β-chlor-δ-nitropyromucic acid is readily soluble in hot water, sparingly soluble in cold water, and crystallises in thick clustered needles. By the slow cooling of the hot solution, or by spontaneous evaporation of the solution, well-formed monoclinic (?) prisms with beveled ends are obtained. The crystallised acid contains one molecule of water, part of which at least it loses over sulphuric acid, and the whole of which may be driven off at 75°. The anhydrous acid melts at 140°–141°.

1.4274 grams air-dried substance lost at 75° 0.1281 gram H_2O.

	Calculated for $C_5H_2ClNO_5.H_2O$.	Found.
H_2O	8.59	8.97

I. 0.2623 gram substance dried at 75° gave 0.1970 gram AgCl.

II. 0.2070 gram substance dried at 75° gave 13.8 cc. of moist nitrogen at 25° under a pressure of 762 mm.

	Calculated for $C_5H_2ClNO_5$.	Found. I.	II.
Cl	18.54	18.57	...
N	7.31	...	7.45

$\beta\gamma$-Dichlor-δ-Sulphopyromucic Acid.

$\beta\gamma$-dichlorpyromucic acid dissolves without charring in fuming sulphuric acid, and in the course of a few hours is converted into the corresponding sulphonic acid. The barium salt obtained by neutralising the diluted solution with baric carbonate is quite readily soluble in cold water, but it can be purified without difficulty by recrystallisation from hot water. The free acid crystallises in distinct radiating needles, and deliquesces rapidly when exposed to the air.

Baric $\beta\gamma$-Dichlor-δ-Sulphopyromucate, $BaC_5Cl_2SO_6.5H_2O$.

This salt is very readily soluble in hot water, less soluble in cold water, and separates as the hot solution cools in globular aggregations of radiating needles which contain five molecules of water. The salt is permanent in the air, but slowly effloresces over sulphuric acid. It loses a part of its water at 100°, but a temperature of 180° appears to be necessary for complete dehydration.

I. 0.4258 gram air-dried salt gave 0.2045 gram $BaSO_4$.
II. 1.0938 grams air-dried salt gave 0.5239 gram $BaSO_4$.
III. 1.5844 grams air-dried salt lost at 185° 0.2930 gram H_2O.
IV. 0.9712 gram air-dried salt lost at 190° 0.1792 gram H_2O.

	Calculated for $BaC_6Cl_2SO_6.5H_2O$.	Found. I.	II.	III.	IV.
Ba	28.19	28.23	28.16	...	...
H_2O	18.52	...	...	18.49	18.45

I. 1.0167 grams salt dried at 185° gave 0.5970 gram $BaSO_4$.
II. 0.6549 gram salt dried at 190° gave 0.3837 gram $BaSO_4$.

	Calculated for $BaC_6Cl_2SO_6$.	Found. I.	II.
Ba	34.59	34.52	34.44

The solubility of the salt in cold water was also determined in the usual manner.

I. 18.7100 grams solution saturated at 18° gave 1.0970 grams $BaSO_4$.

II. 21.2012 grams solution saturated at 18° gave 1.2458 grams $BaSO_4$.

The aqueous solution saturated at 18° therefore contained the following percentages of the anhydrous salt:

I.	II.
9.97	9.98

Plumbic βγ-Dichlor-δ-Sulphopyromucate, $PbC_6Cl_2SO_6.3H_2O$.

The lead salt is readily soluble in hot water, more sparingly soluble in cold water, and separates on cooling its concentrated aqueous solution in masses of fine needles.

I. 0.5342 gram air-dried salt gave 0.3106 gram $PbSO_4$.
II. 0.5524 gram air-dried salt gave 0.3212 gram $PbSO_4$.
III. 1.1523 grams air-dried salt lost at 160° 0.1163 gram H_2O.
IV. 1.2621 grams air-dried salt lost at 160° 0.1286 gram H_2O.

	Calculated for $PbC_6Cl_2SO_6.3H_2O$.	Found. I.	II.	III.	IV.
Pb	39.81	39.72	39.73	...	...
H_2O	10.39	...	...	10.09	10.19

I. 0.4520 gram salt dried at 160° gave 0.2910 gram $PbSO_4$.
II. 0.6342 gram salt dried at 160° gave 0.4107 gram $PbSO_4$.

	Calculated for $PbC_6Cl_2SO_6$.	Found. I.	II.
Pb	44.42	43.98	44.24

Potassic βγ-Dichlor-δ-Sulphopyromucate, $K_2C_5Cl_2SO_6.H_2O$.

This salt we made by precipitation with potassic carbonate from the barium salt. It was readily soluble even in cold water, and crystallised in needles which contained one molecule of water. The air-dried salt lost nothing over sulphuric acid.

I. 0.6161 gram air-dried salt gave 0.3017 gram K_2SO_4.

II. 0.6722 gram air-dried salt gave 0.3299 gram K_2SO_4.

III. 1.4226 grams air-dried salt lost at 160° 0.0686 gram H_2O.

	Calculated for $K_2C_5Cl_2SO_6.H_2O$.	Found. I.	II.	III.
K	22.02	21.99	22.04	...
H_2O	5.07	...	...	4.82

I. 0.6218 gram salt dried at 160° gave 0.3200 gram K_2SO_4.

II. 0.7197 gram salt dried at 160° gave 0.3688 gram K_2SO_4.

	Calculated for $K_2C_5Cl_2SO_6$.	Found. I.	II.
K	23.19	23.10	23.01

The calcium salt of the acid is very soluble even in cold water, and it was not obtained in a crystalline form.

Action of Bromine.

βγ-dichlor-δ-sulphopyromucic acid and its salts are immediately oxidised by bromine in aqueous solution, with the formation of carbonic dioxide, sulphuric acid, and dichlormaleic acid. Baric βγ-dichlor-δ-sulphopyromucate was suspended in water and a slight excess of bromine added. Baric sulphate was at once thrown down, and from the filtered solution dichlormaleic acid was obtained by extraction with ether. From the acid the anhydride was made by sublimation and its identity established through its melting-point, 119° to 120°.[1]

The formation of βγ-dichlor-δ-nitropyromucic acid through the action of fuming nitric acid has already been described by Hill and Jackson.[2]

β-Sulpho-δ-Chlorpyromucic Acid.

δ-chlorpyromucic acid was slowly added to four times its weight of fuming sulphuric acid (sp. gr. 1.95), and the solution allowed to stand for ten or twelve hours. The formation of the sulphonic

[1] Ciamician and Silber: Ber. d. chem. Gesell. **16**, 2396.

[2] This Journal **12**, 126; and Proc. Am. Acad. **24**, 361.

acid was then complete, and on neutralising the diluted solution with baric carbonate a barium salt was obtained which could easily be purified by recrystallisation from hot water. The free β-sulpho-δ-chlorpyromucic acid crystallised in dendritic needles which under ordinary atmospheric conditions are permanent in the air.

Baric β-Sulpho-δ-Chlorpyromucate, $BaC_5HClSO_4.5H_2O$.

This salt is readily soluble in hot water, and but sparingly soluble in cold water. It crystallises in large radiating needles which are permanent in the air, but slowly loses four of its five molecules of water over sulphuric acid.

I. 0.8535 gram air-dried salt gave 0.4411 gram $BaSO_4$.
II. 1.6218 grams air-dried salt gave 0.8371 gram $BaSO_4$.
III. 1.9648 grams air-dried salt lost at 130° 0.3893 gram H_2O.
IV. 0.9748 gram air-dried salt lost at 150° 0.1927 gram H_2O.
V. 1.9953 grams air-dried salt lost at 140° 0.3936 gram H_2O.

	Calculated for $BaC_5HClSO_4.5H_2O$.	Found. I.	II.	III.	IV.	V.
Ba	30.34	30.38	30.35	...	...	...
H_2O	19.93	...	...	19.81	19.76	19.73

1.5355 grams air-dried salt lost over H_2SO_4 0.2467 gram H_2O.

	Calculated for $BaC_5HClSO_4.5H_2O$.	Found.
$4H_2O$	15.95	16.06

I. 1.5480 grams salt dried at 130° gave 0.9992 gram $BaSO_4$.
II. 1.2325 grams salt dried at 140° gave 0.7866 gram $BaSO_4$.

	Calculated for BaC_5HClSO_4.	Found. I.	II.
Ba	37.89	37.96	37.52

The solubility of the salt in cold water was determined in the usual way.

I. 35.0277 grams solution saturated at 18° gave 0.3817 gram $BaSO_4$.

II. 27.2112 grams solution saturated at 18° gave 0.2985 gram $BaSO_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt:

I.	II.
1.69	1.70

Acid Baric β-Sulpho-δ-Chlorpyromucate, $Ba(C_5H_2ClSO_6)_2.4H_2O$.

This salt was made by mixing solutions of the neutral barium salt and the free acid in equivalent quantities. It proved to be quite readily soluble in cold water, much more freely soluble in hot water, and separated on cooling in well-formed rhombic prisms which were permanent in the air and lost nothing over sulphuric acid.

I. 0.6413 gram air-dried salt gave 0.2261 gram $BaSO_4$.

II. 0.6463 gram air-dried salt gave 0.2281 gram $BaSO_4$.

III. 1.7167 grams air-dried salt lost at 125° 0.1855 gram H_2O.

	Calculated for $Ba(C_5H_2ClSO_6)_2.4H_2O$.	Found. I.	II.	III.
Ba	20.76	20.72	20.75	...
H_2O	10.91	...	...	10.81

I. 0.7345 gram salt dried at 125° gave 0.2900 gram $BaSO_4$.

II. 0.7734 gram salt dried at 125° gave 0.3052 gram $BaSO_4$.

	Calculated for $Ba(C_5H_2ClSO_6)_2$.	Found. I.	II.
Ba	23.30	23.21	23.20

The solubility of the salt in cold water was also determined.

I. 6.7510 grams solution saturated at 20° gave 0.1935 gram $BaSO_4$.

II. 5.6625 grams solution saturated at 20° gave 0.1627 gram $BaSO_4$.

The solution saturated at 20° therefore contained the following percentages of the anhydrous salt:

I.	II.
7.23	7.24

Calcic β-Sulpho-δ-Chlorpyromucate, $CaC_5HClSO_6.2H_2O$.

The calcium salt crystallises in transparent prisms which contain two molecules of water. It is permanent in the air or over sulphuric acid, and requires a high temperature for complete dehydration. The salt dried at 200° showed no signs of decomposition.

I. 0.9321 gram air-dried salt gave 0.4166 gram $CaSO_4$.

II. 0.8489 gram air-dried salt gave 0.3784 gram $CaSO_4$.

III. 1.6243 grams air-dried salt lost at 200° 0.1904 gram H_2O.

	Calculated for $CaC_5HClSO_4.2H_2O$.	Found. I.	II.	III.
Ca	13.31	13.14	13.11	...
H_2O	11.98	...	...	11.72

I. 0.5804 gram salt dried at 200° gave 0.2956 gram $CaSO_4$.
II. 0.7000 gram salt dried at 200° gave 0.3566 gram $CaSO_4$.

	Calculated for CaC_5HClSO_4.	Found. I.	II.
Ca	15.12	14.98	14.98

Plumbic β-Sulpho-δ-Chlorpyromucate, $PbC_5HClSO_4.H_2O$.

This salt is sparingly soluble in cold water, more readily soluble in hot water, and crystallises in compact clusters of radiating prisms. It loses nothing over sulphuric acid, or when heated to 100°.

I. 0.5646 gram air-dried salt gave 0.3799 gram $PbSO_4$.
II. 0.6672 gram air-dried salt gave 0.4485 gram $PbSO_4$.
III. 1.6403 grams air-dried salt lost at 165° 0.0705 gram H_2O.
IV. 1.5787 grams air-dried salt lost at 160° 0.0631 gram H_2O.
V. 1.6982 grams air-dried salt lost at 160° 0.0629 gram H_2O.

	Calculated for $PbC_5HClSO_4.H_2O$.	I.	II.	Found. III.	IV.	V.
Pb	46.06	45.95	45.93	...	...	...
H_2O	4.00	...	...	4.29	3.99	3.70

I. 0.5240 gram salt dried at 165° gave 0.3690 gram $PbSO_4$.
II. 1.0133 grams salt dried at 160° gave 0.7118 gram $PbSO_4$.
III. 0.5399 gram salt dried at 160° gave 0.3791 gram $PbSO_4$.

	Calculated for PbC_5HClSO_4.	I.	Found. II.	III.
Pb	47.98	48.10	48.01	47.96

Potassic β-Sulpho-δ-Chlorpyromucate, $K_2C_5HClSO_4$.

The potassium salt crystallises in long needles which are anhydrous.

I. 0.9272 gram air-dried salt gave 0.5309 gram K_2SO_4.
II. 0.8955 gram air-dried salt gave 0.5126 gram K_2SO_4.
III. 0.7962 gram air-dried salt gave 0.4562 gram K_2SO_4.

	Calculated for $K_2C_5HClSO_4$.	I.	Found. II.	III.
K	25.84	25.70	25.70	25.73

Although there could be little doubt that the sulphonic acid formed from δ-chlorpyromucic acid was identical in structure with the β-sulpho-δ-brompyromucic acid of Hill and Palmer,[1] we wished to prove this identity more rigorously by preparing from it by reduction the β-sulphopyromucic acid. We found that the method employed by Hill and Palmer in the reduction of the bromine compound could successfully be employed in this case, although the chlorine was replaced with much greater difficulty, and long-continued boiling of the ammoniacal solution with zinc dust was essential for complete reduction. We also found it advantageous to convert the baric β-sulphopyromucate into the acid salt, and to purify this by recrystallisation from hot water. The neutral salt was crystallised for analysis by evaporation *in vacuo* over sulphuric acid.

I. 0.7039 gram air-dried salt gave 0.4287 gram $BaSO_4$.

II. 1.0434 grams air-dried salt lost at 160° 0.1476 gram H_2O.

	Calculated for $BaC_5H_2SO_5{\cdot}3H_2O$.	Found. I.	Found. II.
Ba	35.96	35.80	...
H_2O	14.18	...	14.15

0.8946 gram salt dried at 160° gave 0.6347 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_5$.	Found.
Ba	41.90	41.72

The solubility of the salt in cold water was determined by the usual method.

I. 14.4785 grams solution saturated at 21° gave 0.1960 gram $BaSO_4$.

II. 12.0525 grams solution saturated at 21° gave 0.1628 gram $BaSO_4$.

The solution saturated at 21° therefore contained the following percentages of the anhydrous salt:

I.	II.
1.90	1.90

These results agree exactly with those obtained by Hill and Palmer for β-sulphopyromucic acid, and the relative position of the sulpho-group is thus established with precision.

[1] This Journal **10**, 409; and Proc. Am. Acad. **23**, 214.

Action of Bromine.

β-sulpho-δ-chlorpyromucic acid is readily oxidised in aqueous solution by bromine, carbonic dioxide is liberated, but little or no sulphuric acid is formed even when the action is long-continued at 100°. With an excess of bromine, an acid is formed which is undoubtedly identical with the sulphofumaric acid described by Hill and Palmer,[1] while a derivative of furfuran-β-sulphonic acid is formed in nearly theoretical quantity, if but a single molecule of bromine is added. For its preparation we passed into a cold aqueous solution of baric β-sulpho-δ-chlorpyromucate the vapor of the calculated weight of bromine by means of a current of air, and evaporated to a small volume the feebly acid solution thus obtained. The barium salt of the αα-chlorbromfurfuran-β-sulphonic acid which was thus obtained could then be purified by recrystallisation. By evaporation in desiccator the free acid was obtained as a waxy deliquescent mass, which showed but slight indications of crystalline structure.

Baric αα-Chlorbromfurfuran-β-Sulphonate,
$Ba(C_4HClBrSO_4)_2.H_2O$.

This salt is readily soluble in hot water, less soluble in cold water, and separates in pearly plates when its hot solution is quickly cooled. A cold solution by spontaneous evaporation deposits this salt in clusters of radiating needles.

I. 0.8479 gram air-dried salt gave 0.2936 gram $BaSO_4$.
II. 0.5210 gram air-dried salt gave 0.1797 gram $BaSO_4$.
III. 1.1406 grams air-dried salt lost at 120° 0.0314 gram H_2O.
IV. 1.6890 grams air-dried salt lost at 138° 0.0491 gram H_2O.

	Calculated for $Ba(C_4HClBrSO_4)_2.H_2O$	Found. I.	II.	III.	IV.
Ba	20.27	20.35	20.28	...	...
H_2O	2.66	...	...	2.75	2.90

I. 0.7017 gram salt dried at 138° gave 0.2496 gram $BaSO_4$.
II. 0.9112 gram salt dried at 138° gave 0.3259 gram $BaSO_4$.
III. 0.7824 gram salt dried at 130° gave 0.2795 gram $BaSO_4$.

	Calculated for $Ba(C_4HClBrSO_4)_2$.	Found. I.	II.	III.
Ba	20.82	20.92	21.03	21.00

[1] This Journal **10**, 414; and Proc. Am. Acad. **23**, 211.

The solubility of the salt in cold water was also determined in the usual way.

I. 20.5274 grams solution saturated at 18° gave 0.3105 gram $BaSO_4$.

II. 21.5098 grams solution saturated at 18° gave 0.3276 gram $BaSO_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt:

I.	III.
4.27	4.30

Calcic aa-Chlorbromfurfuran-β-Sulphonate, $Ca(C_4HClBrSO_4)_2.2H_2O$.

The calcium salt crystallises in large concentrically grouped needles which contain two molecules of water. It is permanent in the air or over sulphuric acid.

I. 0.6429 gram air-dried salt gave 0.1480 gram $CaSO_4$.

II. 0.7372 gram air-dried salt gave 0.1702 gram $CaSO_4$.

III. 0.7580 gram air-dried salt lost at 160° 0.0468 gram H_2O.

	Calculated for $Ca(C_4HClBrSO_4)_2.2H_2O$.	Found. I.	II.	III.
Ca	6.70	6.77	6.79	...
H_2O	6.03	...	...	6.17

I. 0.4463 gram salt dried at 160° gave 0.1097 gram $CaSO_4$.

II. 0.4230 gram salt dried at 165° gave 0.1045 gram $CaSO_4$.

	Calculated for $Ca(C_4HClBrSO_4)_2$.	Found. I.	II.
Ca	7.13	7.23	7.26

Plumbic aa-Chlorbromfurfuran-β-Sulphonate, $Pb(C_4HClBrSO_4)_2.H_2O$.

The lead salt is but sparingly soluble in cold water, and its solubility is but little increased by heat. By evaporation *in vacuo* over sulphuric acid it was obtained in compact hemispherical masses. The salt may be dried without decomposition at 100°, but at a somewhat higher temperature it begins to decompose, and at 140° it is completely charred.

I. 0.5743 gram air-dried salt gave 0.2339 gram $PbSO_4$.

II. 1.5077 grams air-dried salt lost at 100° 0.0410 gram H_2O.

	Calculated for $Pb(C_4HClBrSO_4)_2.H_2O$.	Found. I.	II.
Pb	27.75	27.83	...
H_2O	2.41	...	2.72

0.7187 gram salt dried at 100° gave 0.3000 gram $PbSO_4$.

	Calculated for $Pb(C_4HClBrSO_4)_2$.	Found.
Pb	28.39	28.52

Potassic aa-Chlorbromfurfuran-β-Sulphonate, $KC_4HClBrSO_4$.

The potassium salt is very soluble in hot water, less soluble in cold water. The hot concentrated solution solidifies on cooling, with the separation of small shining anhydrous plates.

I. 0.5801 gram air-dried salt gave 0.1699 gram K_2SO_4.

II. 0.5479 gram air-dried salt gave 0.1625 gram K_2SO_4.

	Calculated for $KC_4HClBrSO_4$.	Found. I.	II.
K	13.05	13.15	13.31

Action of Chlorine.

We attempted to prepare *aa*-dichlorfurfuran-β-sulphonic acid by the action of chlorine upon the salts of β-sulpho-δ-chlorpyromucic acid. We found, however, that the reaction in this case was not as simple as that with bromine, in that oxidation of the furfuran-sulphonic acid began long before one molecule of chlorine had been added, and that sulphofumaric acid and even sulphuric acid were formed before the whole of the original sulphochlorpyromucic acid had disappeared. While it was not difficult to isolate a salt which had substantially the properties and the composition of a baric dichlorfurfuran sulphonate, we were unable to prepare by any variation of the method, a product from which we could obtain perfectly satisfactory results.

Action of Nitric Acid.

We studied the action of nitric acid upon β-sulpho-δ-chlorpyromucic acid, only so far as to satisfy ourselves that no nitro-acid could be formed in this way, and that sulphofumaric acid was the chief product of the reaction.

LXXVII.—ON CERTAIN PRODUCTS OF THE DRY DISTILLATION OF WOOD: METHYLFURFUROL AND METHYLPYROMUCIC ACID.[1]

By Henry B. Hill and Walter L. Jennings.

Several years ago, one of us described[2] the occurrence of furfurol in not inconsiderable quantity among the products of the dry distillation of wood at low and carefully regulated temperatures, as carried on at Brooklyn under the direction of Dr. E. R. Squibb. Although attempts were made at the time to separate by fractional distillation the higher-boiling constituents of the crude furfurol, ordinary boiling-flasks alone were employed, and the results were so far from encouraging that a more thorough investigation was for the moment relinquished. The gradual accumulation of larger quantities of these higher-boiling oils encouraged us to renew the investigation, and we soon found that fractions of constant boiling-point could readily be isolated by using in the distillation the extremely effective bead-columns of Hempel.[3] The most noticeable fraction which we obtained was one boiling at 184°–186°. This proved to contain chiefly methylfurfurol, a preliminary account of which was published[4] soon after its identification. A few months later Maquenne,[5] and Bieler and Tollens,[6] quite independently of each other, found the same methylfurfurol among the products formed by the distillation of several species of seaweed with dilute sulphuric acid, and showed that the fucusol of Stenhouse[7] was a mixture of furfurol with this methylfurfurol. Shortly afterwards the same body was obtained by the action of dilute sulphuric acid upon isodulcite by Maquenne,[8] who pointed out that this mode of formation, taking into consideration the constitution of isodulcite as established by Fischer and Tafel,[9] proved the

[1] A part of the work described in the following paper was presented in the form of a thesis to the Faculty of Arts and Sciences of Harvard University in May, 1892, by Walter L. Jennings, then candidate for the degree of Doctor of Philosophy. The paper was presented at a meeting of the American Academy of Arts and Sciences, held November, 1892.

[2] This Journal **3**, 34; and Proc. Am. Acad. **16**, 155.

[3] Zischr. anal. Chem. **20**, 502.

[4] Ber. d. chem. Ges. **22**, 607.

[5] Comptes rendus **109**, 571.

[6] Ber. d. chem. Ges. **22**, 3062; Ann. Chem. (Liebig) **257**, 110.

[7] Ann. Chem. (Liebig) **74**, 278.

[8] Comptes rendus **109**, 603.

[9] Ber. d. chem. Ges. **20**, 1092; **21**, 2173.

methyl group to be in the δ-position. This conclusion of Maquenne concerning the structure of methylfurfurol was afterward confirmed in this laboratory by a study of the product formed by the action of aqueous bromine upon methylpyromucic acid, and a brief description of this reaction was published at the time.[1] Instead of the half-aldehyde of fumaric acid,

$$C_2H_2\begin{cases}COOH\\COH\end{cases}$$

which is formed under like conditions from pyromucic acid, methylpyromucic acid yields the acetacrylic acid of Wolff,[2]

$$C_2H_2\begin{cases}COOH\\COCH_3\end{cases}$$

and the formation of this ketone acid proves that the methyl group is attached to the δ carbon atom of the furfuran ring. We have also studied the action of dry bromine upon methylpyromucic acid, and have found that a somewhat unstable tetrabromide may be prepared, although the substitution-products are more readily obtainable. For the preparation of the tetrabromide the temperature must be kept below 0°; if the bromine be allowed to act at ordinary temperatures, a brommethylpyromucic acid is formed which melts at 150°–151°, and contains the bromine in the furfuran ring, while at higher temperatures (50°–60°) the bromine enters chiefly the side-chain and forms ω-brommethylpyromucic acid melting at 147°–148°. The formation of these two isomeric products at different temperatures recalls the analogous reactions in the aromatic series, and the analogy is completely borne out by the behavior of the two acids. We have also made a dibrommethylpyromucic acid melting at 175°, in which one bromine atom is situated in the furfuran ring, the other in the side-chain. By the action of water upon the two acids which contain halogen in the side-chain we have made the corresponding oxy-acids.

We had intended to make a thorough study of the higher boiling fractions of the crude furfurol, and to determine as far as possible the nature of the various constituents; but the investigation of the methylfurfurol and its derivatives proved so much more attractive that we have contented ourselves with the partial examination of the fractions boiling at 200°–215° and established in them the presence of guaiacol.

[1] Ber. d. chem. Ges. **23**, 452. [2] *Ibid.* **20**, 426; Ann. Chem. (Liebig) **254**, 245.

METHYLFURFUROL.

The material which we had at our disposal was that portion of the crude furfurol which remained behind at 175° on distilling the oil several times from ordinary retorts or boiling flasks. It had been accumulating for more than ten years, was dark in color, somewhat thick and viscous, and left on distillation a large tarry residue. We therefore distilled it from small copper retorts until signs of decomposition appeared. While the earlier investigations had shown that the temperature could be pushed to over 300° without essential decomposition, we now found that carbonisation ensued at about 250°. At first we ascribed this difference in behavior to decomposition effected by long standing of the material; but we subsequently learned that changes had also been made in the meantime in the factory methods, and that it was quite possible that the greater part of our material had been subjected to the newer treatment. A special examination of the residue yielded by the distillation of nearly fifty kilograms of a fresh supply of crude furfurol showed that in this case decomposition also set in at 250°, so that no products boiling above this temperature could be obtained.

On fractioning with the aid of a Hempel column the yellow distillate which was first obtained, we soon found that it still contained considerable quantities of furfurol, and aside from this, that a comparatively large portion distilled between 180° and 185°, and a smaller portion at 200°–220°. As the distillation progressed, the intermediate fractions diminished in such a way that it became evident that but one body could be isolated between 165° and 200°, and that it boiled at a temperature not far from 185° (uncorrected). We therefore continued the distillation, taking two-degree fractions, and were able to collect a large portion which boiled with satisfactory constancy at 184°–186°. As the material thus obtained showed the character of an aldehyde, a portion of it was shaken with a concentrated solution of acid sodic sulphite. The oil was almost wholly dissolved with the evolution of heat, and as the solution cooled it solidified with the separation of flat radiating prisms. These were drained thoroughly upon the pump, washed with cold alcohol, pressed, and dried. The dry crystals were then decomposed by the requisite amount of sodic carbonate in aqueous solution, and the liberated aldehyde distilled over with

steam. The oil which passed over was then dried with fused calcic chloride and distilled. It showed the constant boiling-point 187°, with the mercury column completely in vapor and under a pressure of 766 mm. The boiling-point of a second preparation was found to be 186.5°–187° under a pressure of 760 mm. An analysis of the oil showed that its formula was $C_6H_6O_2$.

0.1995 gram substance gave 0.4788 gram CO_2 and 0.0998 gram H_2O.

	Calculated for $C_6H_6O_2$.	Found.
C	65.45	65.43
H	5.45	5.56

The formula of the substance, together with its strongly marked resemblance to furfurol, identified it as a methylfurfurol, and by oxidation with moist silver oxide it could readily be converted into the corresponding methylpyromucic acid.[1]

Freshly distilled methylfurfurol is a nearly colorless oil, with an odor closely resembling that of furfurol. On standing it grows dark-colored apparently more rapidly than furfurol, and acquires an acid reaction. The compound which it forms with acid sodic sulphite crystallises in flat concentrically grouped prisms, which are usually rectangularly truncated. The salt dissolves in from two to three parts of water at ordinary temperatures. In the preliminary paper already referred to,[2] the statement was made that methylfurfurol gave the characteristic color reaction with a solution of rosaniline decolorised by sulphurous acid. We have found, however, that carefully purified methylfurfurol gives to this solution but a slight brown-red, or, if added in larger quantity, but a pale wine-red coloration, and are forced to conclude that the color formerly observed was due to a slight admixture of furfurol. It gives, however, with diazobenzol sulphonic acid when tested in the manner described by Penzoldt and Fischer[3] a color identical in shade with that given by furfurol. With hydrochloric acid and resorcin it gives an orange-red, with pyrogallol a carmine-red condensation-product. Aniline acetate paper gives at first no color, or at best turns but a light yellow, but on standing a deep orange color is developed. With phenylhydrazine a liquid hydrazone is formed, which we have not further examined. The specific gravity of methylfurfurol we have found to be somewhat higher than given by Maquenne.[4] A freshly prepared sample made with

[1] See page 165.
[2] *Ibid.* **16**, 657.
[3] Ber. d. chem. Ges. **22**, 607.
[4] Ann. chim. phys. [6] **22**, 84.

great care gave us at 18° referred to water at the same temperature the specific gravity 1.1087, or 1.1072 referred to water at 4°. As the sample was slightly colored it was distilled twice in a stream of hydrogen, but the specific gravity was altered but a few units in the fifth decimal place. The original fraction 186°–187° (cor.) from which this sample was made gave a specific gravity of 1.1059. Maquenne found the specific gravity of his fraction 185°–187° to be 1.107, and of the portion boiling at 187° to be 1.104. In water methylfurfurol is more sparingly soluble than furfurol, and requires about thirty times its weight of water at ordinary temperatures for complete solution.

Since it was difficult to form even an approximate estimate of the relative amounts of furfurol and of methylfurfurol contained in the crude oil from an examination of the residues from previous distillations which we had at our disposal, we submitted to fractional distillation about 50 kilograms of the crude oil. We used a copper retort of eight litres' capacity, which was fitted with a suitable column made out of large thin-walled brass pipe and filled with glass beads. After repeated distillations we obtained about two per cent. of the material taken in the fraction boiling from 182°–186° (uncorrected), and sixty per cent. in the fraction boiling from 160°–165°. Although the absolute amounts doubtless would have been somewhat increased by further separation of the small intermediate fractions, the relative amounts could have been little altered.

Methylfurfuramide, $C_{18}H_{18}N_2O_3$.—An aqueous solution of methylfurfurol, when mixed with ammonic hydrate, gives after the lapse of some time a crystalline precipitate of methylfurfuramide. This substance crystallises in slender radiating needles, dissolves readily in alcohol, ether, chloroform, benzol or carbonic disulphide, but is more sparingly soluble in ligroin. The substance recrystallised from ligroin was found to melt at 86°–87°, and contained the proper percentage of nitrogen.

0.3510 gram substance gave 27.8 cc. of moist nitrogen at 22° and under a pressure of 759 mm.

	Calculated for $C_{18}H_{18}N_2O_3$.	Found.
N	9.03	8.96

Guaiacol.

The larger fractions of the oil boiling above methylfurfurol were those which were collected between 200° and 220°, but even after long-continued distillation no substances of constant boiling-point could be isolated. While the oil did not appear to contain an aldehyde in sensible quantities, a large portion of it was soluble in aqueous alkalies, and we thought it advisable to take advantage of this fact in order to simplify our task. The fractions 200°–215° were therefore united, shaken with a solution of sodic hydrate, and the aqueous emulsion distilled with steam as long as oil passed over. The alkaline solution was then acidified and again distilled with steam. The neutral oil when dried with calcic chloride distilled at 210°–220°, and we have not yet examined it further. The oil which was soluble in the alkaline solution boiled between 200° and 205°, and the thermometer remained for a long time constant at 202°. The physical properties of this oil and the emerald-green color which ferric chloride developed in its alcoholic solution left no doubt in our minds that it was guaiacol, and we thought that it could possibly be most conveniently identified with precision by converting it into the tribromguaiacol of Tiemann and Koppe.[1] [redacted]dding bromine to an alcoholic solution according to their [redacted]ons, however, we obtained an unsatisfactory product. The melting-point, although somewhat higher than that given by Tiemann and Koppe (102°), was not sharp, and was little improved by repeated recrystallisation. As the inherent disadvantages in adding bromine to an alcoholic solution were sufficiently obvious, we substituted glacial acetic acid for the alcohol, and at once obtained a definite product. From 5 grams of our oil we obtained 8.3 grams of a highly crystalline, nearly colorless bromine derivative, which melted at 111°–112°, and a single recrystallisation sufficed to raise the melting-point to 115°–116°. Further recrystallisation from alcohol or benzol failed to raise this melting-point. While our product thus melted 14° higher than the tribromguaiacol of Tiemann and Koppe, it agreed in other respects with their description, and the following analyses show that it had the same composition:

I. 0.2316 gram substance gave 0.1974 gram CO_2 and 0.0345 gram H_2O.

[1] Ber. d. chem. Gesell. **14**, 2017.

II. 0.1603 gram substance gave 0 2497 gram AgBr.
III. 0.1705 gram substance gave 0.2653 gram AgBr.

	Calculated for $C_7H_4Br_2O_2$.	Found. I.	II.	III.
C	23.27	23.25	...	...
H	1.39	1.65	...	...
Br	66.48	...	66.30	66.24

Since we had failed to identify our substance as guaiacol through the melting-point of this bromine derivative, we proceeded to prepare from it pyrocatechin. For this purpose we used, instead of the more usual hydriodic acid, hydrochloric acid, as W. H. Perkin, Jr.[1] had recently shown the decomposition was in this case nearly perfect if the reaction took place in sealed tube at 170°–180°. On opening the tube, a gas escaped which burned with a green-bordered flame. The aqueous solution was extracted with ether, and the crystalline residue which was left upon evaporating the ether was distilled. The substance boiled at 240°–242°, and the solidified distillate melted at 103°–104°. When recrystallised from benzol it formed colorless lustrous scales, which appeared under the microscope to be rectangular plates, and melted sharply at 104°. The boiling-point of pyrocatechin is usually given at 240°–245°, and the melting-point was found by Fittig and Mager[2] to be 104°. In aqueous solution our product also gave with ferric chloride an emerald-green coloration which turned to a violet-red on the addition of sodic carbonate. It was thus established with precision that pyrocatechin had been formed by heating with hydrochloric acid the oil under investigation, and the latter was therefore in its turn identified as guaiacol. It seems to us probable that the tribromguaiacol which we have just described is identical with that of Tiemann and Koppe, and that the low melting-point which they observed was due to by-products introduced by their method of preparation. A more extended investigation of the matter was, however, wholly foreign to our line of work. We hope that the constituents of the crude furfurol which boil above 200° may be studied more fully in this laboratory at some future time.

Methylpyromucic Acid.

In order to prepare from methylfurfurol the corresponding methylpyromucic acid, we first attempted to follow the methods

[1] J. Chem. Soc. **57**, 589. [2] Ber. d. chem. Ges. **8**, 365.

which we had already used in the manufacture of pyromucic acid from furfurol. We found, however, that alkaline hydrates, either in alcoholic or aqueous solution,[1] gave us an extremely poor product in very unsatisfactory quantity. Although the experiments of Lessing in the laboratory of Limpricht[2] upon the oxidation of furfurol with argentic oxide gave us little hope that we could in this way conveniently prepare large quantities of methylpyromucic acid, no better method suggested itself to us at the time, and we were forced to adopt it. To our surprise, we found that we could easily obtain in this way a weight of methylpyromucic acid which nearly equaled that of the aldehyde taken, and that we could also obtain from furfurol under the same conditions an equally satisfactory yield of pyromucic acid. From methylfurfurol we obtained as a maximum 84 per cent. of the theoretical yield of methylpyromucic acid, from furfurol 82 per cent. of the calculated amount of acid. As the weight of acid remaining in solution after precipitation with hydrochloric acid was in neither case taken into account, the reaction may fairly be called quantitative. The large yield which we obtained was doubtless due in part to a slight modification of the ordinary method of procedure, which we shall presently describe. Still we had no difficulty in obtaining from 10 grams of furfurol in the usual way 8.5 grams of argentic pyromucate, and from the acidified mother-liquor by extraction with ether 2.9 grams of pyromucic acid, so that the total yield of pyromucic acid in this case was 7.25 grams, or 62.1 per cent. of the theoretical amount.

[1] For many years a concentrated aqueous solution of sodic hydrate has been used at this laboratory in the preparation of pyromucic acid. Our method has been, however, essentially different from that recommended by H. Schiff (Ann. Chem. (Liebig) **239**, 374; **261**, 254), in that we have destroyed the furfuryl alcohol by hydrochloric acid instead of removing it with ether. The saving of time and of ether has more than compensated us for the somewhat diminished yield. 2 litres of furfurol are very gradually mixed with 1200 cc. of aqueous sodic hydrate (1 : 1), taking care by constant stirring and cooling that the thick paste does not grow hot. On the following day 2 litres of concentrated hydrochloric acid are gradually added, the temperature toward the end being allowed to rise somewhat to facilitate the complete decomposition of the furfuryl alcohol. If the temperature rises too rapidly the reaction becomes violent. The furfuryl alcohol is in any case converted into a tough leathery substance, which grows brittle on standing with the excess of hydrochloric acid. The slightly colored mother-liquor is drained off, the residue crushed in an iron mortar, 4 litres of water added, and then calcic hydrate, until the solution is permanently alkaline. After standing for several days, the solution being kept slightly alkaline, the pyromucic acid is carried completely into solution. The filtrate is but slightly colored, and this slight color may be almost wholly removed by bone-black. The yield of nearly colorless pyromucic acid which may be obtained in this way amounts to from 35 to 40 per cent. of the weight of furfurol taken.

[2] Ann. Chem. (Liebig) **165**, 279. Lessing obtained a weight of pyromucic acid equal to but 14 per cent. of the weight of furfurol employed, or but 12 per cent. of the theoretical amount.

All the methylpyromucic acid which we have used in our investigations we have made by the following method. 10 grams of methylfurfurol were added to about 50 grams of well-washed argentic oxide suspended in about 800 cc. of hot water, and the whole heated quickly to boiling. When the reaction appeared to be complete, pure sodic carbonate was added in quantity sufficient to precipitate the silver which had been carried into solution, and the feebly alkaline solution again boiled. When the fresh well-marked reduction which then ensued was finished, the solution was filtered, evaporated to small volume, again filtered, and acidified with hydrochloric acid. The acid which separated as the solution cooled was nearly colorless, and as a rule a single recrystallisation was sufficient to raise the melting-point to the proper point. The slight color could be most conveniently removed, if necessary, by treating a solution of the calcium salt with bone-black.

0.2067 gram of the acid gave 0.4321 gram CO_2 and 0.0900 gram H_2O.

	Calculated for $C_6H_4O_3$.	Found.
C	57.14	57.01
H	4.76	4.84

Methylpyromucic acid melts at 108°–109°, and sublimes readily at low temperatures. It is readily soluble in alcohol, ether, chloroform, or hot benzol, more sparingly soluble in cold benzol, and almost insoluble in carbonic disulphide. It is extremely soluble in hot water, and on cooling it separates from concentrated solutions in short, thick six-sided prisms, or in small six-sided plates formed by the development of these prisms parallel to the basal plane. From dilute solutions it frequently separates in feathery or bladed aggregations. The solubility of the acid in cold water we determined by titration with a standard solution of baric hydrate, using phenolphthalein as an indicator.

I. 22.293 grams of a solution saturated at 20° required for neutralisation 15.3 cc. of a solution of baric hydrate, containing 0.01864 gram BaO_2H_2 in 1 cc.

II. 19.665 grams of a solution saturated at 20° required for neutralisation 13.55 cc. of the above solution of baric hydrate.

According to these determinations an aqueous solution saturated at 20° contained the following percentages of acid:

I.	II.
1.89	1.89

Methylpyromucic acid is therefore decidedly less soluble in water at ordinary temperatures than pyromucic acid.[1]

For the further characterisation of the acid we have prepared a number of its salts.

Baric methylpyromucate, $Ba(C_6H_5O_3)_2$.—This salt we made by boiling an aqueous solution of the acid with baric carbonate. The salt is readily soluble in cold water, somewhat less soluble in hot water, and separates on evaporation in small colorless octahedral crystals which are anhydrous. The salt thoroughly dried by pressure suffered no material loss of weight on exposure to the air.

I. 0.3366 gram air-dried salt gave 0.2023 gram $BaSO_4$.

II. 0.4261 gram air-dried salt gave 0.2562 gram $BaSO_4$.

	Calculated for $Ba(C_6H_5O_3)_2$.	Found. I.	II.
Ba	35.40	35.34	35.34

The solubility of the salt in water at ordinary temperatures we determined in the usual way.

I. 5.8353 grams of a solution saturated at 19.6° gave 0.7950 gram $BaSO_4$.

II. 5.5326 grams of a solution saturated at 19.6° gave 0.7526 gram $BaSO_4$.

According to these determinations, the aqueous solution saturated at 19.6° contained the following percentages of the salt:

I.	II.
22.62	22.59

In order to determine the solubility at higher temperatures we followed essentially the method recommended by V. Meyer.[2]

I. 6.8590 grams of a solution saturated at 99° gave 0.8655 gram $BaSO_4$.

II. 5.1805 grams of a solution saturated at 99° gave 0.6480 gram $BaSO_4$.

The aqueous solution saturated at 99° therefore contained the following percentages of the salt:

[1] According to Houton Labillardière (Ann. chim. phys. [2], **9**, 368), pyromucic acid is soluble in 26 parts of water at 15°. This result is confirmed by approximate determinations made in this laboratory as a guide in the preparation of pyromucic acid. It was found that 100 cc. of a solution saturated at 17° contained 3.35 grams of the acid, and that 100 cc. of a saturated solution of sodic chloride at the same temperature dissolved 0.60 gram of the acid. The erroneous statement made in the preliminary description of the acid (Ber. d. chem. Gesell. **22**, 608), that it was "somewhat more readily soluble in water" than pyromucic acid, was based upon rough quantitative results obtained in recrystallising from water the small quantity of the acid which I then had at my disposal.—H. B. H.

[2] Ber. d. chem. Ges. **8**, 1002.

I.	II.
20.95	20.78

Calcic methylpyromucate, $Ca(C_6H_5O_4)_2.2H_2O$.—The calcium salt is readibly soluble in cold water, and the solubility is slightly increased by heat. It crystallises in clusters of long radiating needles which contain two molecules of water.

I. 0.3544 gram air-dried salt gave 0.1475 gram $CaSO_4$.

II. 0.3184 gram air-dried salt gave 0.1333 gram $CaSO_4$.

III. 0.8481 gram air-dried salt lost at 110° 0.0931 gram H_2O.

IV. 0.5421 gram air-dried salt lost at 110° 0.0596 gram H_2O.

	Calculated for $Ca(C_6H_5O_4)_2.2H_2O$.	Found. I.	II.	III.	IV.
Ca	12.28	12.24	12.31	...	...
H_2O	11.04	...	...	10.97	10.99

I. 0.2688 gram salt dried at 110° gave 0.1254 gram $CaSO_4$.

II. 0.3109 gram salt dried at 110° gave 0.1452 gram $CaSO_4$.

	Calculated for $Ca(C_6H_5O_4)_2$.	Found. I.	II.
Ca	13.79	13.72	13.74

In determining the solubility of the salt, the calcium was precipitated as oxalate and weighed as sulphate.

I. 6.8529 grams of a solution saturated at 20.2° gave 0.4104 gram $CaSO_4$.

II. 7.8851 grams of a solution saturated at 20.2° gave 0.4688 gram $CaSO_4$.

The aqueous solution saturated at 20.2° therefore contained the following percentages of the anhydrous salt:

I.	II.
12.77	12.68

Argentic methylpyromucate, $AgC_6H_5O_4$.—This salt may readily be made by precipitation of a soluble salt with silver nitrate, and may be recrystallised from hot water. It is sparingly soluble even in boiling water, and crystallises from aqueous solution in fine slender needles.

I. 0.2110 gram salt gave on ignition 0.0977 gram Ag.

II. 0.4007 gram salt gave on ignition 0.1855 gram Ag.

	Calculated for $AgC_6H_5O_4$.	Found. I.	II.
Ag	46.34	46.30	46.29

Sodic methylpyromucate, $NaC_6H_5O_3$.—The sodium salt is exceedingly soluble even in cold water. It separated from its solution in dilute alcohol after long standing in compact clusters of small anhydrous needles.

I. 0.2752 gram air-dried salt gave 0.1325 gram Na_2SO_4.

II. 0.4240 gram air-dried salt gave 0.2043 gram Na_2SO_4.

	Calculated for $NaC_6H_5O_3$.	Found. I.	II.
Na	15.53	15.60	15.53

Potassic methylpyromucate, $KC_6H_5O_3$.—The potassium salt is also very readily soluble in cold water, and crystallises in spherical aggregations of short prisms which appear to be anhydrous.

0.3385 gram air-dried salt gave 0.1790 gram K_2SO_4.

	Calculated for $KC_6H_5O_3$.	Found.
K	23.83	23.74

Ethyl methylpyromucate, $C_6H_5O_3C_2H_5$.—The ethyl ether of the acid we made in the ordinary way, by saturating a solution in an equal weight of absolute alcohol with hydrochloric acid. The excess of hydrochloric acid was then driven off at a gentle heat, the ether precipitated with water, washed with a dilute solution of sodic carbonate, dried with calcic chloride and distilled. The whole product passed over between 212° and 215°, and by far the greater portion showed the constant boiling-point 213°–214° with the mercury column completely in vapor under a pressure of 766 mm. The ether showed no tendency toward crystallisation when cooled with ice and salt.

I. 0.2363 gram substance gave 0.5404 gram CO_2 and 0.1392 gram H_2O.

II. 0.1570 gram substance gave 0.3585 gram CO_2 and 0.0921 gram H_2O.

	Calculated for $C_6H_5O_3C_2H_5$.	Found. I.	II.
C	62.34	62.36	62.27
H	6.49	6.54	6.52

Methylpyromucamide, $C_6H_5O_2NH_2$.—Ethyl methylpyromucate is readily attacked by concentrated aqueous ammonia, and the reaction is completed in the cold after the lapse of two days. The clear solution then yields on evaporation the corresponding amide in long colorless prisms which melt at 131°. It is readily soluble in alcohol, dissolves freely in hot benzol or ligroin, sparingly in

the cold, and may best be recrystallised from hot water, in which it is readily soluble.

I. 0.2207 gram substance gave 22.8 cc. of moist nitrogen at 28° and under a pressure of 762 mm.

II. 0.1839 gram substance gave 19.1 cc. of moist nitrogen at 26° and under a pressure of 751 mm.

	Calculated for $C_6H_5O_2NH_2$.	Found. I.	II.
N	11.20	11.36	11.38

Action of Bromine and Water.

Although Maquenne[1] had shown that the ready formation of methylfurfurol from isodulcite led directly to the conclusion that it must contain its methyl group in the δ position, it seemed desirable to establish this point by independent facts. Since pyromucic acid could readily be oxidised by bromine in aqueous solution, and converted into well marked bodies of the maleic acid group, it seemed probable that methylpyromucic acid would also yield analogous products. It was soon found that homogeneous products could not easily be obtained by using an excess of bromine, as is the case with pyromucic acid. Although a crystalline derivative could be obtained under certain conditions, the yield was not satisfactory, and viscous products were also formed. With two molecules of bromine, however, it was easy to reach definite results. Limpricht[2] showed in 1873 that pyromucic acid could be converted into a body which he called the half-aldehyde of fumaric acid, by the action of two molecules of bromine upon its aqueous solution, and v. Baeyer[3] subsequently proved that fumaric acid could be formed from this by the action of argentic oxide. It was evident, if methylpyromucic acid was decomposed in an analogous fashion, that there should be formed either an homologous aldehyde acid, or a ketone acid, according to the position of the methyl group in the furfuran ring. The formation of a ketone aldehyde under these conditions did not seem possible since Hill and Sanger[4] had shown that the aldehyde group in analogous reactions is invariably formed from the δ carbon of the pyromucic acid. The product formed from methylpyromucic acid under these conditions proved to be a ketone acid, and a brief description of the results of a preliminary examination which was undertaken at

[1] Comptes rendus **109**, 603.
[2] Ann. Chem. (Liebig) **165**, 285.
[3] Ber. d. chem. Ges. **10**, 1362.
[4] Proc. Am. Acad. **21**, 185.

the time by Mr. W. S. Hendrixson[1] and one of us was published elsewhere about two years ago. For the sake of completeness an account of these preliminary experiments will be included in the description of our own work, and we also owe to Mr. Hendrixson the analytical data which we publish. If methylpyromucic acid is suspended in about fifteen times its weight of cold water, and the vapor of bromine is slowly passed in by means of a current of air, the color of the bromine is quickly discharged, and the acid goes into solution with the escape of carbonic dioxide. When exactly two molecules of bromine have been added, the whole is allowed to stand for a short time, and the colorless solution then thoroughly extracted with ether. The ether left upon evaporation a crystalline body which was recrystallised from boiling benzol, and finally from water. An analysis showed that the formula of the substance was $C_5H_6O_2$.

0.2461 gram substance gave 0.4734 gram CO_2 and 0.1185 gram H_2O.

	Calculated for $C_5H_6O_2$.	Found.
C	52.64	52.47
H	5.26	5.35

The new body was readily soluble in hot water, more sparingly soluble in cold water, and was acid in its character. It dissolved readily in alcohol, ether, or boiling chloroform, more sparingly in cold chloroform. In hot benzol it was quite readily soluble, and very sparingly soluble in cold benzol, carbonic disulphide, or ligroin. It crystallised in long slender lustrous needles, which melted at 122°–123°. Recrystallisation from various solvents failed to raise the melting-point, but after several careful sublimations it melted at 123°–124°. The formula of this acid was further controlled by an analysis of its silver salt, which was prepared by the cautious addition of ammonic hydrate to a solution of the acid containing argentic nitrate. The salt can be recrystallised from boiling water without difficulty, and forms concentrically clustered six-sided plates.

I. 0.2237 gram salt gave 0.1901 gram AgBr.

II. 0.2926 gram salt gave 0.2484 gram AgBr.

	Calculated for $AgC_5H_5O_2$.	Found. I.	Found. II.
Ag	48.87	48.81	48.76

[1] Ber. d. chem. Ges. **23**, 452.

The acid which had thus been formed from methylpyromucic acid corresponded well with the description of the acetacrylic acid which Wolff[1] had shortly before made through the decomposition of β-bromlaevulinic acid. Its melting-point, however, was given by Wolff as 125°–125.5°, although he adds in a more recent paper[2] that impurities otherwise imperceptible may depress the melting-point from two to three degrees. In order to compare the two acids, we have ourselves made the acetacrylic acid of Wolff from β-bromlaevulinic acid. In the preparation of the β-bromlaevulinic acid we followed with precision the directions of Wolff. The complete purification of the crude acid was in our hands attended with great loss of time and material, and, even after repeated recrystallisation from carbonic disulphide, we failed to raise the melting-point above 58°, while Wolff gives 59° as the melting-point of the pure acid. Under these circumstances we did not attempt to prepare pure β-bromlaevulinic acid in larger quantity, but decomposed with sodic acetate in an acetic acid solution a preparation which melted at 55°–56°. The acetacrylic acid which we thus obtained was to all appearance identical with that made from methylpyromucic acid. As was to be expected, its melting-point was somewhat low, 121°–123°, but after several recrystallisations from benzol melted at 123°–124°. Wolff[3] describes the silver salt of his acid as stellate needles, while the silver salt of our acid crystallised in well-formed six-sided plates. We convinced ourselves that the same six-sided plates were formed by the addition of argentic nitrate to a moderately concentrated solution of both acids, and that on recrystallisation these plates frequently formed dendritic aggregations. These dendritic forms only were seen if an insufficiently purified acid was used. While it is very possible that the acids which we had in our hands were in neither case absolutely pure, we cannot doubt the identity of the material from the two sources.

In order to identify still further our product with Wolff's acetacrylic acid, we dissolved it in chloroform and added at low temperature one molecule of bromine. The color of the bromine was discharged, and on evaporation a crystalline residue was obtained which melted after recrystallisation from a mixture of benzol and carbonic disulphide at 107°–108°. According to Wolff,[2] the αβ-dibromlaevulinic acid melts at this point. With phenylhydrazine

[1] Ber. d. chem. Gesell. **20**, 426. [2] Ann. Chem. (Liebig) **264**, 245. [3] *Ibid.* p. 248.

our product also readily gave the corresponding hydrazone, identical in every respect with the body described by Bender[1] and shortly afterward by Decker.[2] It crystallised in small yellow prisms, which melted at 156°–157°, and dissolved in concentrated sulphuric acid with a red color. Analysis showed that it had the formula $C_{11}H_{12}N_2O_2$.

I. 0.2240 gram substance gave 0.5299 gram CO_2 and 0.1190 gram H_2O.

II. 0.2173 gram substance gave 26.6 cc. of moist nitrogen at 23° and under a pressure of 752 mm.

	Calculated for $C_{11}H_{12}N_2O_2$.	Found. I.	Found. II.
C	64.71	64.52	...
H	5.88	5.90	...
N	13.73	...	13.64

Bromine in aqueous solution, therefore, converts methylpyromucic acid into acetacrylic acid according to the equation

$$C_6H_6O_3 + 2Br_2 + 2H_2O = C_5H_6O_2 + CO_2 + 4HBr.$$

The formation of this ketone acid from methylpyromucic acid, while pyromucic acid under the same conditions yields an aldehyde acid, shows conclusively that the methyl group of the methylpyromucic acid stands in the δ place.

Action of Concentrated Sulphuric Acid.

We have thought that it might be possible to bring additional evidence as to the structure of the methylpyromucic acid through an investigation of the sulphonic acid derived from it. A study of the sulphonic acids derived from pyromucic acid had already shown that δ-sulphonic acids were always formed by the action of fuming sulphuric acid whenever the δ-hydrogen had not already been otherwise replaced; when the δ-hydrogen had been thus replaced, β-sulphonic acids were formed. Moreover, it was very easy to distinguish between the two isomers, in that bromine in aqueous solution instantly formed sulphuric acid from the δ-sulphonic acids, while the β-sulphonic acids were oxidised to products which retained the sulpho group. Methylpyromucic acid was added with careful cooling to three times its weight of fuming sulphuric acid, the whole allowed to stand for twenty-four hours,

[1] Ber. d. chem. Gesell. **21**, 2494. [2] *Ibid.* **21**, 2937.

and the diluted solution then neutralised with baric carbonate as usual. The barium salt which was obtained by evaporating the filtered solution crystallised in long needles, which were frequently collected in globular aggregations. The salt was hardly more soluble in hot than in cold water, and could best be obtained by the evaporation of its cold aqueous solution *in vacuo* over sulphuric acid. In this respect it closely resembled the baric β-sulphopyromucate. An analysis showed that the salt was baric sulphomethylpyromucate, and that it contained five molecules of water of crystallisation.

I. 0.4798 gram air-dried salt gave 0.2597 gram $BaSO_4$.

II. 0.6678 gram air-dried salt lost at 165° 0.1383 gram H_2O.

	Calculated for $BaC_6H_4SO_6\ 5H_2O$.	Found. I.	Found. II.
Ba	31.78	31.83	...
H_2O	20.87	...	20.71

0.5272 gram salt dried at 165° gave 0.3598 gram $BaSO_4$.

	Calculated for $BaC_6H_4SO_6$.	Found.
Ba	40.17	40.13

Bromine water gave in an aqueous solution of the salt no precipitate even on boiling, but after this treatment with bromine, if baric hydrate was added to alkaline reaction, a white flocculent precipitate, which closely resembled baric sulphofumarate, appeared. This behavior showed conclusively that the sulpho group had not entered the furfuran ring in the δ-position, and the conclusion seems warranted that it had not done so only because the methyl group already occupied that place.

Brommethylpyromucic Acids.

Bromine acts readily upon methylpyromucic acid at ordinary temperatures, and substitution is so easily effected that the isolation of an addition-product is a matter of considerable difficulty. The instability of the addition-product renders it unsuitable for the preparation of substituted acids, and facilitates the formation of satisfactory products by direct substitution. The nature of the products thus formed is, however, largely dependent upon the temperature at which the reaction takes place. At low temperatures the bromine enters first the furfuran ring and afterwards the methyl group, while at higher temperatures the methyl group is

first attacked, although substitution apparently takes place at the same time to a certain extent in the ring. The facts which we have observed evidently correspond precisely with those so thoroughly established in the aromatic series. Moreover, those bodies which contain the halogen in the side-chain are extremely susceptible to double decomposition, and are even decomposed by heating for a short time with water. The halogen in the main ring, on the other hand, is held quite as persistently as that in the corresponding derivatives of pyromucic acid. The study of these bodies presented at first many difficulties, the solution of which cost us so much time and labor that we have been unable to carry our researches as far as we had hoped. Since one of us must now relinquish the work, we shall present the results we have obtained, although they are in many respects incomplete. Further researches upon the subject will be made in this laboratory. We are especially sorry that we have been unable to determine with precision the place in which the bromine enters the furfuran ring; while we have obtained by oxidation of the brommethylpyromucic acid in question an acid which is doubtless a bromacetacrylic acid, we have not yet been able to establish its structure and thus make it available in determining the constitution of the brommethylpyromucic acid from which it is formed. There can be but little doubt, however, that the bromine in this case enters the β-position, as it does with pyromucic acid itself as soon as the δ-hydrogen atom is replaced by bromine.

β(?)-Brommethylpyromucic Acid.

When dry bromine acts at ordinary temperatures upon methylpyromucic acid, hydrobromic acid is at once evolved, and brommethylpyromucic acid is formed. The reaction is most readily controlled by the use of a solvent, and we have found glacial acetic acid most convenient for the purpose. We have found it necessary to add decidedly more than one molecule of bromine, and the best results were obtained by using three atoms. The methylpyromucic acid is dissolved in one and a half times its weight of glacial acetic acid (99.5 per cent.), and the necessary amount of bromine carefully added, taking care that the temperature does not rise above 17°. After standing for some time at ordinary temperatures, the greater part of the hydrobromic acid

is expelled *in vacuo* over lime, the residue poured into water, and the acid extracted with ether. The crude acid left on the distillation of the ether we have found it most advantageous to convert into the sodium salt with alcoholic sodic hydrate. The sodium salt is easily collected upon a filter, and the acid is then reprecipitated from its aqueous solution after decolorisation with bone-black. The acid may be further purified by several repetitions of the same process.

I. 0.2279 gram substance gave 0.2935 gram CO_2 and 0.0526 gram H_2O.

II. 0.1147 gram substance gave 0.1055 gram AgBr.

	Calculated for $C_6H_5BrO_2$.	Found. I.	II.
C	35.12	35.13	...
H	2.44	2.56	...
Br	39.02	...	39.15

Brommethylpyromucic acid crystallises in colorless branching needles, which melt at 150°–151°. It is readily soluble in alcohol, ether, or chloroform, somewhat sparingly soluble in cold, more readily in hot benzol. In carbonic disulphide or ligroin it dissolves but sparingly even on boiling. It is somewhat sparingly soluble in hot water, and is deposited in clusters of branching needles as the solution cools. The solubility of the acid in water at ordinary temperatures we determined in the usual way. We neutralised with baric carbonate the solution of the acid, and determined as sulphate the barium which had been dissolved.

I. 17.598 grams of a solution saturated at 21.4° gave 0.0271 gram $BaSO_4$.

II. 16.031 grams of a solution saturated at 21.4° gave 0.0264 gram $BaSO_4$.

The aqueous solution saturated at 21.4° therefore contained the following percentages of the acid:

I.	II.
0.27	0.29

For the further characterisation of the acid we also prepared certain of its salts.

Baric brommethylpyromucate, $Ba(C_6H_4BrO_3)_2.4H_2O$.—This salt may readily be made from a solution of the ammonium salt by precipitation. It is sparingly soluble in cold water, more readily soluble in hot water, and crystallises from the hot aqueous solution

on cooling in dendritic needles, which contain four molecules of water. The salt is permanent in the air, but effloresces rapidly over sulphuric acid.

I. 0.4478 gram air-dried salt gave 0.1690 gram $BaSO_4$.

II. 0.8747 gram air-dried salt lost at 110° 0.1030 gram H_2O.

	Calculated for $Ba(C_6H_4BrO_3)_2.4H_2O$.	Found. I.	II.
Ba	22.20	22.19	...
H_2O	11.67	...	11.78

0.3664 gram salt dried at 110° gave 0.1558 gram $BaSO_4$.

	Calculated for $Ba(C_6H_4BrO_3)_2$.	Found.
Ba	25.14	25.00

The solubility of the salt in cold water was determined in the usual way.

I. 19.211 grams of a solution saturated at 20.2° gave 0.0518 gram $BaSO_4$.

II. 19.984 grams of a solution saturated at 20.2° gave 0.0466 gram $BaSO_4$.

The aqueous solution saturated at 20.2° therefore contained the following percentages of the anhydrous salt:

I.	II.
0.63	0.55

Calcic brommethylpyromucate, $Ca(C_6H_4BrO_3)_2.3H_2O$.—The calcium salt we prepared by precipitating with calcic chloride an ammoniacal solution of the acid. It crystallised from hot water in clusters of short needles which contained three molecules of water. The salt was permanent in the air, and lost but little in weight over sulphuric acid.

I. 0.2508 gram air-dried salt gave 0.0680 gram $CaSO_4$.

II. 0.5443 gram air-dried salt lost at 110° 0.0584 gram H_2O.

	Calculated for $Ca(C_6H_4BrO_3)_2.3H_2O$.	Found. I.	II.
Ca	7.97	7.98	...
H_2O	10.76	...	10.73

0.2724 gram salt dried at 110° gave 0.0584 gram $CaSO_4$.

	Calculated for $Ca(C_6H_4BrO_3)_2$.	Found.
Ca	8.93	8.86

In determining the solubility of the salt the calcium was precipitated as oxalate, and converted into sulphate before weighing.

I. 15.373 grams of a solution saturated at 20° gave 0.0189 gram $CaSO_4$.

II. 13.879 grams of a solution saturated at 20° gave 0.0170 gram $CaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt:

I.	II.
0.41	0.40

Argentic brommethylpyromucate, $AgC_6H_4BrO_3$.—The silver salt crystallises from hot water is spherical aggregations of dendritic needles.

0.0956 gram salt gave 0.0574 gram AgBr.

	Calculated for $AgC_6H_4BrO_3$.	Found.
Ag	34.61	34.48

Potassic brommethylpyromucate, $KC_6H_4BrO_3$.—This salt is very readily soluble even in cold water, and crystallises on slow evaporation of its aqueous solution in small anhydrous needles.

0.2789 gram salt gave 0.0993 gram K_2SO_4.

	Calculated for $KC_6H_4BrO_3$.	Found.
K	16.08	15.99

Action of Bromine and Water.

The whole behavior of the brommethylpyromucic acid showed conclusively that its bromine atom was situated in the furfuran ring. Although the bromacetacrylic acids had not yet been made, one of which would doubtless be formed by the oxidation of this brommethylpyromucic acid, and we therefore could not hope to determine whether the bromine was in the β or in the γ position, we nevertheless thought it best to investigate the products of oxidation. Brommethylpyromucic acid was suspended in thirty times its weight of water, and somewhat more than two molecules of bromine then slowly passed in by means of a current of air. The acid was readily carried into solution, and at the same time a small amount of an insoluble substance was formed. The filtered solution was extracted with ether, and the ethereal extract dried with calcic chloride. The viscous residue which was left on the distillation of the ether gradually solidified on standing over sulphuric acid *in vacuo*. This body proved to be an acid, containing bromine, readily soluble in water, but crystallising from benzol by evapora-

tion in rosettes. The melting-point of the recrystallised acid was found to be 61°. An analysis showed that the percentage of bromine contained in this acid agreed with that required by a bromacetacrylic acid.

0.1630 gram substance gave 0.1594 gram AgBr.

	Calculated for $C_4H_3BrO_3$.	Found.
Br	41.45	41.62

The oxidation had therefore taken precisely the same direction as that followed by the analogous decomposition of methylpyromucic acid, and through this product of oxidation it will doubtless be possible at some future time to fix the constitution of the brommethylpyromucic acid. A product apparently identical with this we have also obtained by the action of dilute nitric acid.

The insoluble product formed at the same time with the bromacetacrylic acid we unfortunately have not been able to study further. It is not acid in its character, contains a large amount of bromine, and crystallises from benzol in long colorless prisms, which melt at 90°–91°.

ω-Brommethylpyromucic Acid.

Although bromine in acting upon methylpyromucic acid at ordinary temperatures enters at once the furfuran ring, at the temperature of boiling carbonic disulphide or chloroform it attacks chiefly the methyl group, and a bromine derivative is formed in considerable quantity which differs wholly in its properties from the acid just described. The reaction is not perfectly simple, for we have found that we could obtain the best yield of the new product by using twice the theoretical quantity of bromine. We have dissolved the methylpyromucic acid in six times its weight of chloroform and slowly added to the boiling solution two molecules of bromine diluted with its own weight of chloroform. The evolution of hydrobromic acid at once begins, and frequently before the bromine is all added a heavy crystalline body separates from the hot solution. When the reaction is over, the chloroform is well cooled, the crystalline product, which amounts to about sixty per cent. of the weight of methylpyromucic acid taken, filtered off, and washed with cold chloroform. It may then be recrystallised from boiling chloroform or benzol.

I. 0.2152 gram substance gave 0.2758 gram CO_2 and 0.0490 gram H_2O.

II. 0.1176 gram substance gave 0.1079 gram AgBr.

	Calculated for $C_6H_5BrO_3$.	Found. I.	II.
C	35.12	34.95	...
H	2.44	2.53	...
Br	39.02	...	39.04

The ω-brommethylpyromucic acid crystallises in small clustered oblique plates which melt at 147°–148°. It is readily soluble in alcohol, ether, glacial acetic acid, or acetone, somewhat sparingly soluble in boiling benzol or chloroform, from which solvents it crystallises well on cooling. In boiling toluol it is freely soluble, sparingly soluble in the cold, and almost insoluble in carbonic disulphide. It is but slowly acted on by cold water, but on warming it is readily dissolved with decomposition. The solution contains hydrobromic acid in abundance, and upon evaporation a crystalline acid is obtained, which is free from bromine. This behavior, which is in such striking contrast with the extreme stability of the derivatives of pyromucic acid that contain halogen, sufficiently establishes the position of the bromine in the side-chain. It also effectually prevented the preparation of its salts by the ordinary methods.

Decomposition by Water.

The product formed by the action of water upon ω-brommethylpyromucic acid we have studied a little more in detail. After heating an aqueous solution for some time at 100° it was evaporated over lime *in vacuo*. The hard black crystalline residue was dissolved in hot water, filtered from the separated carbon, and again evaporated. The brownish vitreous crystalline mass thus obtained melted with decomposition at 158°–162°, and by recrystallisation from a mixture of toluol and absolute alcohol the melting-point could be raised to 162°–163°, although the body still melted with decomposition. A combustion showed that the substance was ω-oxymethylpyromucic acid.

0.2623 gram substance gave 0.4870 gram CO_2 and 0.1052 gram H_2O.

	Calculated for $C_6H_4O_4$.	Found.
C	50.70	50.63
H	4.23	4.46

ω-Oxymethylpyromucic acid is readily soluble in water, alcohol, or glacial acetic acid. In ether it is but slightly soluble, and in benzol, toluol, chloroform, or carbonic disulphide it is almost wholly insoluble. The barium salt of the acid is readily soluble in water, and is left as a varnish as its aqueous solution evaporates. From concentrated solutions it is thrown down as a flocculent precipitate on the addition of alcohol. We have not yet examined it further, and we have as yet found no other salts of a more inviting character.

The ease with which the ω-brommethylpyromucic acid entered into reaction with water naturally suggested the study of its behavior with other reagents. Unfortunately, we are unable to pursue our investigations in this direction, but further researches will be made in this laboratory.

In the preparation of the ω-brommethylpyromucic acid small quantities of the isomeric acid were also apparently formed. From the chloroform mother-liquors we obtained, after treatment with water and baric carbonate, a small amount of a crystalline acid which melted at 149°–151°, and in other respects resembled the brommethylpyromucic acid first described.

ωβ(?)-Dibrommethylpyromucic Acid.

If the brommethylpyromucic acid melting at 150°–151° is treated with bromine in boiling chloroform, a second atom of bromine enters the side-chain and a dibrommethylpyromucic acid is formed. The acid which separates on cooling or after partial evaporation of the solvent is washed with cold chloroform, and recrystallised from boiling toluol. This acid may perhaps more economically be made by the direct action of bromine at ordinary temperatures. Methylpyromucic acid is exposed over night to the vapor of three times its weight of bromine. The semi-liquid product is well washed with carbonic disulphide, next with chloroform, and the crystalline residue recrystallised from boiling toluol. Our analyses are not altogether satisfactory, but they leave no doubt as to the nature of the body.

I. 0.2877 gram substance gave 0.2735 gram CO_2 and 0.0418 gram H_2O.

II. 0.2086 gram substance gave 0.2748 gram AgBr.

	Calculated for $C_6H_4Br_2O_3$.	Found. I.	II.
C	25.35	25.92	...
H	1.41	1.61	...
Br	56.33	...	56.07

This dibrommethylpyromucic acid crystallises in small oblique tabular crystals, which melt at 175° with decomposition. It is readily soluble in alcohol, ether, or glacial acetic acid, is but sparingly soluble in boiling benzol or chloroform, and almost insoluble in carbonic disulphide or ligroin. In boiling toluol it is quite readily soluble.

Action of Water.

On warming with water the acid is decomposed, hydrobromic acid is formed, and the solution then contains an oxybrommethylpyromucic acid. We prepared this acid first by treating with water the product formed by the vapors of bromine upon methylpyromucic acid, and separating it from the brommethylpyromucic acid melting at 151° which accompanied it by washing the mixed acids with benzol. The acid thus prepared from the crude material was absolutely identical with that afterwards made from the pure dibrommethylpyromucic acid. For analysis the substance was crystallised from a mixture of benzol and alcohol.

I. 0.1950 gram substance gave 0.2333 gram CO_2 and 0.0420 gram H_2O.

II. 0.1695 gram substance gave 0.1445 gram AgBr.

	Calculated for $C_6H_5BrO_4$.	Found. I.	II.
C	32.58	32.63	...
H	2.26	2.39	...
Br	36.20	...	36.28

The ω-oxy-β(?)-brommethylpyromucic acid is readily soluble in alcohol and ether, very sparingly soluble in boiling carbonic disulphide, somewhat more readily soluble in boiling chloroform, from which it separates on cooling in obliquely terminated prisms. It is sparingly soluble in hot benzol, and almost insoluble in ligroin. It is readily soluble in hot water, more sparingly in cold, and separates from dilute aqueous solutions in large obliquely terminated prisms, which contain one molecule of water. The crystals effloresce slowly over sulphuric acid, or even in the air after months of exposure, but we were unable to dehydrate them by heat without bringing about slight decomposition.

I. 0.4413 gram of acid crystallised from water lost over sulphuric acid 0.0328 gram H_2O.

II. 0.2117 gram of acid dried in desiccator over night gave 0.1681 gram AgBr.

	Calculated for $C_6H_5BrO_4.H_2O$.	Found. I.	II.
H_2O	7.53	7.43	...
Br	33.47	...	33.80

The anhydrous acid melts at 153°–154°, and on cooling forms a viscous gummy mass. Sodium amalgam reduces the acid without difficulty, and yields the ω-oxymethylpyromucic acid already described. The barium salt of the acid is readily soluble in water, and crystallises in clustered short needles, but we have made no further study of its salts.

Methylpyromucic Tetrabromide.

We have already spoken of the instability of the addition product which methylpyromucic acid forms with bromine. We succeeded in isolating it by adding two molecules of bromine diluted with a little chloroform to a solution of methylpyromucic acid in five times its weight of chloroform well cooled with ice and salt. The bromine was slowly added with constant shaking, and at this low temperature but little hydrobromic acid was noticed. The addition-product soon began to separate in flat colorless needles, which were frequently twinned at right angles. After the bromine had all been added, the whole was allowed to stand for a short time, and the product then quickly filtered upon the pump and washed with cold chloroform. It was then pressed with filter-paper and dried in desiccator. As we found it impossible to recrystallise the substance without serious decomposition, we analysed it without further purification. On exposure to moist air it rapidly liquefied, and even over sulphuric acid it soon evolved hydrobromic acid in abundance. Analyses IV and V made with material which had stood for two and four days respectively in desiccator, show how rapidly the decomposition progresses.

I. 0.2695 gram substance gave 0.1668 gram CO_2 and 0.0383 gram H_2O.

II. 0.3509 gram substance gave 0.2182 gram CO_2 and 0.0467 gram H_2O.

III. 0.2011 gram substance freshly made gave 0.3393 gram AgBr.

IV. 0.1564 gram of same substance after two days gave 0.2601 gram AgBr.

V. 0.1520 gram of same substance after four days gave 0.2513 gram AgBr.

	Calculated for $C_6H_8Br_4O_2$.	Found. I.	II.	III.	IV.	V.
C	16.14	16.88	16.96	...	...	...
H	1.35	1.58	1.48	...	...	...
Br	71.74	...	...	71.81	70.79	70.37

Methylpyromucic tetrabromide is very sparingly soluble in carbonic disulphide or ligroin, somewhat less sparingly soluble in chloroform or benzol. In hot chloroform or benzol it dissolves more freely, but decomposition evidently ensues, for little unaltered substance crystallises on cooling. The substance melts at about 95° with decomposition, but the melting-point varies with the rapidity with which it is heated. Although the addition-product is so unstable, we have been able to find but few definite products resulting from its decomposition. Alcoholic sodic hydrate apparently destroys it completely. Sodic acetate in glacial acetic acid gives the brommethylpyromucic acid melting at 150°–151°, and the same acid also appears to be formed in the spontaneous decomposition of the body when exposed to the air.

Further investigation in this direction will be made in this laboratory.

Contributions from the Chemical Laboratory of the U. S. Department of Agriculture. Sent by H. W. Wiley.

XXII.—MOVEMENT OF THE ELEMENT PHOSPHORUS IN THE MINERAL, VEGETABLE, AND ANIMAL KINGDOMS, AND THE BIOLOGICAL FUNCTION OF THE LECITHINES.

By W. Maxwell.

In a preceding article[1] treating of the "Role of the Lecithines in Normal Germination," an endeavor was made to show the mode of movement of the element phosphorus, and the function of the

[1] This Journal **13**, 16.

lecithine bodies, during the period of germination and incipient growth of vegetable organisms.

Given varieties of seeds were selected, and in each of these the proportions of phosphorus present as mineral, in the form of phosphates, and likewise as organic phosphorus, in the form of lecithines, were determined. In the next place, further quantities of the same seeds were germinated, and the relative proportions of mineral and organic phosphorus in the germinated product redetermined. Three terms were observed in the period of germination, the last indicating the stage in the initial growth when the plantlet had consumed the whole of the reserve-material of the mother-seed, and was prepared to attach itself to extraneous matters for support.

The examinations of the products of germination of the several terms showed that the phosphorus which was contained in the original, or mother-, seed as a mineral phosphate had gradually decreased, and finally disappeared; and further, that in the proportion in which the decrease had occurred in the phosphorus present as phosphate, an increase had taken place in the amount of organic phosphorus observed in the form of lecithine.

It was thus shown that the organism of the seed possesses the property of eliminating the phosphorus from the mineral combination as a phosphate, and of causing it by a reorganisation to occur as a member of an organic molecule. It was likewise shown that the lecithine bodies are not only a medium by which the element phosphorus passes over from the mineral to the vegetable kingdom, but that the phosphorus taken up by the plant as a phosphate in aqueous solution is very probably in the first place converted into the form of an organic compound, and afterwards incorporated and utilised by the organism.

Having followed the movement of the element phosphorus from the mineral into the vegetable kingdom, it became of great moment and interest to investigate its mode of passage from the vegetable to the animal kingdom, and also to note any continued function of the lecithine bodies as a medium of transmission.

An investigation of the direct mode of passage of the element from the vegetable to the animal, upon the lines followed in the observation of its movement from the mineral to the vegetable, presented difficulties of a severe character; and in particular, the impossibility of controlling the conditions, and establishing terms

of development, such as were noted in the first part of the work. In view of these difficulties it was decided to select an animal organism in which the element phosphorus was contained in the mineral form as a phosphate, and likewise as a lecithine, corresponding to the mode of appearance of the element in the seed organism, and to pursue the movements and behavior of the element in processes and conditions analogous to those obtaining in vegetable germination.

The hen's egg was selected as the organism and material of the second part of the investigation. Not only does the egg contain phosphorus in inorganic combinations, but very notable quantities of lecithines are present as a significant constituent of the yolk. Moreover, the nature of the egg, and the inclosure of the processes and products of incubation very chiefly within the walls of the shell, fully provide for the control of conditions essential to the work.

The plan of the investigations conducted with the egg was in close resemblance to that adopted in the vegetable part of the work. In the first place, the relative proportions of phosphorus contained in the normal egg as mineral phosphate and lecithine respectively, were determined. Secondly, the eggs were incubated, the process of incubation being checked at specific terms of development of the embryo, and the relative amounts of mineral and organic phosphorus determined in the products of incubation. By such a plan of procedure the proportion, and the mode of combination of the phosphorus in the natural egg were, in the first place, ascertained. Also the relative proportions contained in mineral and organic forms at each stage of the period of incubation, and the movements of the element were observed during the time of progression of the embryo from the initial term to the time of leaving the shell.

The incubation was accomplished in the incubators in operation in the laboratory of the Bureau of Animal Industry, and under the direction of Dr. Theobald Smith, to whose courtesy the author was materially indebted.

The eggs were weighed before and after incubation, and the loss of substance which had occurred by the processes incident to the initial life of the embryo was determined. The weights of a given number of eggs before, after partial, and at the end of mature, incubation, are given in the following table:

Series I.

Egg.	Before Incubation.	After 15 days Incubation.	Loss of Weight.
No. 1.	58.66 grams.	49.74 grams.	15.21 per cent.
No. 2.	54.67	46.95	14.15
No. 3.	66.19	56.10	15.25
			Mean = 14.90

Series II.

Egg.	Before Incubation.	After Mature Incubation.	Loss of Weight.
No. 1.	57.72 grams.	48.40 grams.	17.58 per cent.
No. 2.	50.42	40.85	19.00
No. 3.	51.79	42.20	18.71
			Mean = 18.43

The ratio of loss of weight of the egg (including the shell[1]) during the process of incubation bears a close resemblance to the loss of substance occurring in vegetable germination; the loss in the latter being somewhat greater than in the former.

Preliminary work was done, with the eggs which had been incubated for the purpose of determining the loss of weight, in order to test the method of extraction and analysis, which method may be briefly given as follows:

In the treatment of the natural egg, the whole contents of the shell, including the white and yolk, were brought into an Erlenmeyer flask and boiled for 6 hours with absolute alcohol under a condenser. The alcoholic extract was distilled off and the residue extracted for 10 hours with ether. The egg material, which had been already boiled with alcohol, was reduced to a state of the greatest possible fineness in a mortar, and re-extracted for 10 hours with ether. The alcohol and ether extracts, containing the whole of the lecithine bodies present in the egg, were brought together and evaporated to a residue. The fatty residue was mixed with alkali salts and ignited, by which means the phos-

[1] A decrease in the substance of the shell had very evidently occurred, and in one particular place. At a period of advanced development, it was observed that the membrane enveloping the embryo was attached to the inner surface of the shell, and at the place of attachment the shell had become noticeably thin, indicating that a decomposition of the lime carbonate had been effected by the action of the animal ferments, or the carbon dioxide disengaged in the processes of incubation. The latter gas, both from the shell and the organic tissues, would escape through the pores of the shell; the calcium, however, could not escape, and it is reasonable to suppose that it was utilised at a later period by the organism in the formation of bone.

phorus, present in the organic form as a lecithine, was converted into phosphates of sodium and potassium. The phosphorus, converted thus from an organic into an inorganic compound, was estimated in the usual way as magnesium pyrophosphate, and the lecithine-content calculated from the amount of pyrophosphate by means of the Hoppe-Seyler[1] factor.

The terms at which the incubation was stopped were as follows:

1. After 12 days incubation.
2. After 17 days incubation.
3. After 20 days incubation.

The temperature of the incubation during the period of incubation was 38°–40° C.

In the first place, a table showing the proportion of phosphorus present in the normal egg, as phosphate and lecithine respectively, will be considered.

Normal Egg.

Egg.	Weight of Egg.	Pyrophosphate whose source was Mineral.	Pyrophosphate whose source was Organic.	Lecithines in Egg.
No. 1.	65 grams.	0.1240 gram.	0.1852 gram.	2.07 per cent.
No. 2.	58	0.1018	0.1375	1.89
No. 3.	66	0.1307	0.1804	1.99

Mean = 1.98

The organism of the egg contains a very notable quantity of lecithine, the mean of the given examples being 1.98 per cent. of the weight of the egg.

I.—*Term of Incubation.*

Egg.	Weight of Egg.	Pyrophosphates whose source was Mineral.	Pyrophosphates whose source was Organic.	ecithines in Egg.
No. 1.	56 grams.	0.1644 gram.	0.0855 gram.	1.11 per cent.
No. 2.	58	0.1623	0.1090	1.43
No. 3.	54	0.1435	0.0848	1.14

Mean of the three examples = 1.22

At the close of the first term, when the incubation had proceeded 12 days, a decrease of 38.7 per cent. is observed in the lecithine-content of the egg. It is also seen that in proportion as the amount of lecithine decreased, the mineral phosphorus, or phos-

[1] Handbuch der physiol. und pathol. chem. Analyse, S. 169.

phate, increased. The uniform behavior of the eggs, which is shown by the almost equal loss of each in the lecithine-content, may be ascribed to their freshness, and that they were the product of only two hens; the smaller eggs being produced by the one and larger eggs by the other.

II.—*Term of Incubation.*

Egg.	Weight of Egg.	Pyrophosphate whose source was Mineral.	Pyrophosphate whose source was Organic.	Lecithines in Egg.
No. 1.	56 grams.	0.1447 gram.	0.1003 gram.	1.30 per cent.
No. 2.	58	0.1395	0.1140	1.45

Mean of the two examples = 1.38

The table indicates that during the longer period of incubation a less decrease in the content of lecithines had taken place. In the first examples, when the period of incubation had been 12 days, 38.7 per cent. of these bodies had disappeared. At the end of 17 days incubation the eggs were found to contain 70.0 per cent. of the original content of lecithines, the actual loss being only 30.1 per cent.

The results obtained in the study of incubation-products of the period of 17 days were not in the direction anticipated. It is apparent that the process of converting the phosphorus of the lecithine bodies into phosphates had ceased in the organism, and that a portion of the phosphates, already formed at the expense of the organic phosphorus, had reverted to the lecithine form; otherwise the organism had increased the content of lecithines by the use of the original phosphates present in the normal egg, converting the phosphorus of those phosphates, in the first place, into organic phosphorus bodies, or lecithines, in order to be used by the organism in the same mode and for the same purpose as the original lecithines. The latter is distinctly the more probable.

The results which were obtained with the products from the 17 days period of incubation are in close agreement, however, with the observations made by Professor Hoppe-Seyler and his pupils. He conducted his studies with the yolk of the egg, in which the lecithines are located, and determined the lecithines, or organic phosphorus, only, taking no cognisance of the mineral phosphorus present in the normal egg. The results obtained by Hoppe-Seyler[1] are given as follows:

[1] Handbuch der physiol. Chemie, S. 782 (Berlin, 1877).

Lecithines contained in yolk of natural egg, 10.720 per cent.
Lecithines after 10 days incubation, 8.406 per cent.
Lecithines after 17 days incubation, 10.677 per cent.

Hoppe-Seyler found that during the first 10 days of incubation almost 22 per cent. of the lecithines had disappeared, and that at the end of 17 days the lecithine-content was almost as great as the amount found in the yolk of the normal egg. At that period his investigations stopped.

As has been stated in the present work, the products of incubation were obtained and studied at the period of maturity of the living organism.

On the twenty-first day of incubation the chicken was removed from the shell. The organism of the bird was mature; every portion of the egg constituents had become converted into living substance. The bird was within one day of leaving the shell. The substance of the bird was prepared for analysis by cutting up wholly, including the flesh, bone, intestines and feathers; no particle being excluded. The extraction of the flesh and bone of bird with alcohol and ether was conducted according to the method already given.

III.—*Term of Incubation.*

Egg.	Weight of Egg.	Pyrophosphate whose source was Mineral.	Organic.	Lecithines in Egg.
No. 1.	65 grams.	0.2515 gram.	0.0793 gram.	0.88 per cent.
No. 2.	64	0.2325	0.1000	1.13

Mean of two examples = 1.00

So far the tables have shown the different proportions of lecithines found in the products at the end of each of the several terms of incubation. But in proportion as the phosphorus contained in the form of lecithine disappeared from the organism, in the same proportion the phosphates, or mineral phosphorus, were found to increase. The following table gives the actual proportions of phosphorus which were found relatively in the mineral and organic forms at the several terms of incubation.

Material.	Organic Phosphorus. Pyrophosphate.[1]	Per cent.	Mineral Phosphorus. Pyrophosphate.	Per cent.
Natural Egg	0.1677 gram =	58.5	0.1188 gram =	41.5
No. 1 Incubation	0.0931 =	37.1	0.1567 =	62.9
No. 2 Incubation	0.1072 =	43.0	0.1421 =	57.0
No. 3 Incubation	0.0896 =	27.0	0.2419 =	73.0

[1] The determinations of pyrophosphate were made by T. C. Trecot.

The analytical data contained in the above table show that, during the period of development of the embryo, as indicated by the several terms at which the process of incubation was checked, the phosphorus had become eliminated from the molecule in which it was present in the natural egg, and incorporated within a mineral body, appearing as a phosphate. That result indicates a reversion of the mode of change which was observed to occur in the vegetable organism under the action of the processes of germination. It was there established that the mineral phosphorus contained in the organism of seeds was converted from the mineral into the organic form, the phosphates being thus utilised in the formation of lecithines. The organism of the chicken during the period of its initial development breaks up the lecithine bodies, and uses the phosphorus in the formation of bone.

In the formation of the phosphate, which is the chief substance of bone, there are two other sources from which very minute portions of phosphorus might be drawn, *viz.* the albuminoid bodies containing phosphorus, the so-called nucleins, and the shell of the egg, which latter would be expected to furnish an appreciable portion of phosphate. The data obtained, however, from the analysis of the shell indicate that it could not contribute more than a trace of phosphorus (although considerable calcium) to aid the animal organism in the formation of bone. The mean of analysis of three shells gave only 0.014 gram pyrophosphate, or 0.16 per cent. of the weight of the shell. It is thus clear that the portion of phosphorus set free by the action of the animal ferments upon the inner surface of the shell during the period of incubation must be so small as not to enter into the present calculations.

It is necessary to conclude that the lecithine bodies furnish the phosphorus which is utilised by the organism in the formation of bone. This conclusion rests not only upon the high percentage of lecithines contained in the natural egg, but also upon the observation that the gradual increase of mineral phosphorus which marks the development of the embryo is accompanied by a proportional decrease in the phosphorus present as lecithine.

The lecithines are a source of the phosphorus required by the animal organism in the formation of bone. These bodies are also a medium by which the phosphorus present in vegetable organisms is received by the animal organism. Most vegetable growths

contain lecithines, and consequently the latter are consumed in animal diet.

The data obtained in the present studies contribute certain indications which bear upon the question: Are the lecithines found in the animal organism such as have been taken up in vegetable food as lecithines, or are they formed by the organism from other bodies containing phosphorus?[1] Returning to the vegetable part of the investigations, it was observed that the phosphates present in the natural seed furnished the phosphorus which was utilised by the embryo plantlet in the formation of lecithines. It was also indicated that the mineral phosphates taken up by the plant in aqueous solution from the earth, and which are seen in the tissues of the plant in crystallised form by use of the microscope, are the source and reserve-material out of which the lecithines are formed, and that the mineral phosphorus is thus first converted into a member of an organic molecule before being incorporated by the plant organism.

In the second part of the work it has been shown that the animal organism uses the lecithine bodies as the source of phosphorus required in the formation of bone. It was also indicated in the examination of the incubation-products of the second term of development that the embryo organism of the chicken had converted a portion of the mineral phosphorus originally found in the egg into lecithine phosphorus, which latter underwent a reorganisation and was utilised by the organism as a constituent of bone. For, as it has previously been maintained, it was extremely improbable, and in the reverse direction of the mode of physiological development, that any portion of an ultimate constituent of the organism should be disintegrated. Consequently, the source of the phosphorus contained in the increment of lecithines found in the incubation-products specified, and found also by Professor Hoppe-Seyler at the same period of development of the embryo, was the original phosphates present in the normal egg.

It has thus been shown that the animal organism possesses the power of converting the phosphorus of mineral phosphate into the phosphorus of lecithine, and also of breaking up those lecithines, eliminating the phosphorus and engaging it as a constituent of bone. And by the data obtained it has been shown that the

[1] See Handbuch der physiol. Chemie, G. Bunge, S. 82.

lecithines found in the animal body may have been formed by the organism within itself, out of mineral phosphates.

It has been shown by A. Bokáy[1] that the lecithine bodies contained in food are very rapidly resolved by the animal ferments into fatty acids, cholin and phosphorus glycerine. It is, then, highly improbable that any portion of the lecithines escapes dissolution under the action of alimentary solvents, and that any part of the lecithines found in the brain and nerve system, and in the several secretions of the animal body, is received and incorporated directly from animal diet. The lecithines taken up by the animal from milk and vegetable foods, and which, it has been shown, are resolved rapidly into the given decomposition-products, doubtless furnish the phosphorus required in the formation of bone before and after the birth of the young animal. On the other hand, it has been shown that the lecithines found in the several regions of the animal body are synthetic products of the organism, the phosphorus being derived from the mineral phosphates taken up by the system in food.

The investigations of Prof. Miescher,[2] which have come to the notice of the author since the present work was begun, led to conclusions which support and are supported by the data which have been recorded. It is known that salmon fish, previous to the period of propagation, move from sea water up into the fresh streams of rivers. The duration of the breeding season extends over several months. During that season the fish consume no food, the alimentary canal always being found empty. Consequently it was observed that the substance required by the organism of the fish for the physiological processes incident to the production of young must be drawn from given regions and materials of the organism of the fish itself. Miescher, in his studies, showed by comparative determinations that the increase in the substance and weight of the ovary was at the expense of a proportional decrease in the weight of the muscular tissue. He observed also that the ova are very rich in nuclein and particularly lecithines, but the muscular tissue extremely poor in these bodies. The tissues of the muscles, however, were very rich in phosphorus, which was present in the form of phosphates. Miescher

[1] Ztschr. physiol. Chem. **1**, S. 158; 1887.

[2] "Statistische und biologische Beiträge zur Kenntniss vom Leben des Rheinlachses." Archiv für Anat. und Physiol., 1881. See note, page 195.

thus came to the conclusion that the lecithines found in great amount in the ova were formed by the organism out of the proteids, fats and phosphates contained by and forming the muscular tissue.

The investigations have shown, finally, that the lecithines exercise the function of receiving phosphorus from minerals and bestowing it in the processes of the animal organism in the formation of bone. These bodies are thus a medium through which the element performs its movements and circulation from the mineral, through the vegetable, and into the animal kingdom.

Contributions from the Chemical Laboratory of Purdue University.

VII.—NOTES ON XYLOSE.

By W. E. Stone and W. H. Test.

The extraction from vegetable tissues of materials which upon hydrolysis yield one or both of the pentose sugars is familiar to students of the carbohydrates. These materials, to which the general name pentosans has been assigned, seem to be abundant. By boiling many vegetable substances with a dilute alkali, such as sodic or calcic hydrate, the pentosans go into solution, from which they may be precipitated by acidulation and addition of alcohol. In this manner Allen and Tollens obtained a substance from wheat-straw from which xylose was easily made by inverting with dilute sulphuric acid.[1] Such a process is, however, an uninviting task when attempted with the ordinary laboratory appliances, owing to the large amount of material required for a small amount of product.

In the manufacture of paper from straw, the straw is boiled for some hours with quick-lime, or, according to an improved process, the straw and quick-lime are placed in large rotating digesters and subjected to the action of steam under high pressure for some hours. From the paper-maker's standpoint this bleaches and disintegrates the fiber of the straw. After the digestion is complete the alkaline liquor is discharged. We have found this

[1] Ber. d. chem. Ges. **23**, 137.

extract a convenient material from which to obtain xylose, as the following notes indicate.

The liquor, after allowing suspended materials to settle, was clear and of a yellowish brown color, with a decided alkaline reaction. The specific gravity by Mohr's balance was 1.215. By titration with half-normal hydrochloric acid different samples showed an alkalinity equivalent to 2–2.5 per cent. of calcium oxide. Upon evaporating 100 cc. in a platinum dish, a thick viscous mass remained which with difficulty could be brought to a constant weight. This residue amounted to 3.95 per cent. of the liquor. By ignition 30.77 per cent. remained, leaving 69.23 per cent. of the solids as organic matter.

Some of the liquor which had been concentrated to one-half its volume by evaporation, was acidulated with hydrochloric acid and received one and one-half volumes of 95-per cent. alcohol, when a dense flocculent precipitate was thrown down. This was dissolved in water and reprecipitated with alcohol three times. Finally the precipitate was strained, pressed dry and placed in large desiccators over sulphuric acid. The material was of a pearly gray color, amorphous, with a tendency to blacken if left exposed to the air. It was, as its further examination showed, the mother-substance of xylose or xylan. From 32 liters of the straw liquor we obtained about 300 grams of xylan. In spite of the attempts at purification it still contained 8.57 per cent. of ash, of which 6.13 per cent. was calcium oxide.

Upon distillation with hydrochloric acid and titration of the distillate with phenylhydrazine in the manner proposed by one of us,[1] the xylan yielded in different determinations 45.5 and 47.1 per cent. of furfurol.

Some attempts were made to ascertain if it were possible to hydrolyse this material by the use of small amounts of acid as has been done by Wohl in the case of inulin;[2] but different modifications of Wohl's method failed to give satisfactory results, and we judge that xylan is far less sensitive to hydrolytic action than inulin.

Hydrolysis was therefore effected in the usual way by heating during eight or ten hours with eight parts of 2-per cent. sulphuric acid. The acid solution was neutralised, evaporated to a syrup, extracted with alcohol and the alcoholic solution again concen-

[1] J. Anal. and Appl. Chem. **5**, No. 8. [2] Ber. d. chem. Ges. **23**, 2084.

trated to a syrup which soon crystallised. After purification the product weighed 35 grams, or a little more than 1 per cent. of the liquor employed and over 10 per cent. of the xylan treated.

The product was identified as xylose by its specific rotation = $(a)_D = +18.4°$, and by the phenylhydrazine compound which melted at 158° and was distinctly laevo-rotatory.[1] It also possessed the other less characteristic properties of xylose.

A second portion of the straw-liquor has been hydrolysed directly without the preliminary precipitation and purification of the xylan, and has given equally good results. It presents, therefore, a convenient source of xylose, the employment of which is preferable to the preparation of the crude material in the laboratory.

The multi-rotation of xylose has been studied by Tollens and Parcus,[2] and we are able to confirm their results by observations upon this material. Two grams of the purified xylose were dissolved in cold water and quickly brought into the polariscope. Only four minutes elapsed between the addition of the water to the sugar and the first reading. The rotatory power decreased very rapidly, as is shown by the following five readings, taken as rapidly as they could be made and recorded:

1. $+14°\ 2' = (a)_D\ 71.65°$
2. $+13°\ 56' =$ " $69.65°$
3. $+13°\ 12' =$ " $66.00°$
4. $+12°\ 24' =$ " $62.00°$
5. $+12°\ 8' =$ " $60.65°$

The readings were begun at 6.30 A. M. and continued at hourly intervals until they became constant. The decrease, which at first was very rapid, was practically at an end after three hours.

Four minutes after solution:

6.30 A. M.,	$(a)_D = 71.65°$	12.30 P. M.,	$(a)_D = 18.95°$
7.30 "	" $= 27.76°$	1.30 "	" $= 18.85°$
8.30 "	" $= 21.22°$	2.30 "	" $= 18.75°$
9.30 "	" $= 18.95°$	3.30 "	" $= 18.40°$
10.30 "	" $= 18.95°$	4.30 "	" $= 18.40°$
11.30 "	" $= 18.95°$		

[1] Ber. d. chem. Ges. **23**, 355.

[2] Ann. Chem. (Liebig) **257**, 175.

ON AMIDOPHOSPHORIC ACID.

By H. N. Stokes.

By replacing the hydroxyls of orthophosphoric acid successively by amido groups, three amides may be derived, namely, amidophosphoric acid, $PO.NH_2.(OH)_2$, diamidophosphoric acid, $PO.(NH_2)_2.OH$, and phosphoryl triamide, $PO(NH_2)_3$, and from these, by abstraction of water or ammonia, an imido acid, PO.NH.OH, an imido amide, $PO.NH.NH_2$, and a nitrile, PO.N. Of these, amido- and diamidophosphoric acids have not yet been described. In the dictionaries of Fehling [1] and of Ladenburg [2] the formula $PO.NH_2.(OH)_2$ is given to a body described by Schiff [3] and called by him *phosphaminsaeure*. This rests on an error of the compilers, as Schiff gives to his acid the formula PO.NH.OH, with which his analyses agree, while they differ widely from that of amidophosphoric acid. Moreover, as will be shown, amidophosphoric acid is a body of entirely different properties.

Schiff [4] also describes the triamide, $PO(NH_2)_3$. Although his analyses agree quite well with this formula, the existence of the body is called in question by Gladstone,[5] who, in repeating Schiff's method of preparation, treating phosphorus oxychloride with dry ammonia, was unable to replace the third chlorine atom at any temperature below that at which further decomposition occurs (above 300°). The correctness of the formula PO.NH.OH assigned by Schiff to his phosphamic acid is also questioned by Gladstone and Holmes,[6] who point out the general resemblance of its properties, as described, to those of pyrophosphodiamic acid, obtained by them. They regard it as a mixture of the latter with metaphosphoric acid. The identity of Schiff's acid with pyrophosphodiamic acid (diamidopyrophosphoric acid) has also found acceptance in some handbooks.[7]

The imido amide, $PO.(NH).NH_2$, was described by Gerhardt [8] under the name phosphamide, and was obtained by treating phos-

[1] Neues Handwörterbuch der Chemie **5**, 423.
[2] Handwörterbuch der Chemie **9**, 100.
[3] Ann. Chem. (Liebig) **103**, 168.
[4] Ann. Chem. (Liebig) **101**, 300.
[5] Journ. Chem. Soc. [2] **7**, 18.
[6] Journ. Chem. Soc. [2] **2**, 229, 235.
[7] Gmelin-Kraut: Handbuch der anorg. Chemie **1**, 2 Abth. 529; Graham-Otto: Anorg. Chem. (Michaelis) **2**, 401.
[8] Ann. chim. phys. [3] **18**, 183.

phorus pentachloride with dry ammonia and then with water. Its nature has not been questioned.

The body PO.N, described by Gerhardt[1] as biphosphamide, by Schiff[2] as monophosphamide, and by Gladstone[3] as phosphonitryle, is the final product of heating the triamide, the imidoamide or the amido chlorides. Its constitution is not known, but is probably much more complex than is represented by the formula given.

In addition to the above, Gladstone and Holmes[4] have obtained a series of complex amides, derivable from pyro- and tetraphosphoric acids.

The difficulty in preparing amido orthophosphoric acids lies in part in the impossibility of regulating the decomposition by water or acids of the products of the action of ammonia on phosphorus pentachloride and oxychloride. Gerhardt's imidoamide and Schiff's triamide seem to be capable of giving ammonia and phosphoric acid only; at least no mention is made of intermediate products. The bodies derived from phosphorus oxychloride by partial replacement of chlorine by amido groups are so decomposed by water as to give the amidopyrophosphoric acids of Gladstone, and further action results in the separation of ammonia before the pyrophosphoryl group is broken up. The reason for this, as will be seen below, lies in the great ease with which amidophosphoric acid passes over into ammonium phosphate. As phosphorus pentoxide is a derivative of pyrophosphoric acid, it is not to be expected that it would give orthophosphoric amides with ammonia.

I have overcome these difficulties in part, by acting with ammonia on phosphoric ethers, and in this way have obtained the primary amide, $PO.NH_2.(OH)_2$. Attempts to obtain other amides by the same method are in progress.

By dissolving the chloride of diphenylphosphoric acid, $PO.Cl.(OC_6H_5)_2$, in alcohol, and adding alcoholic ammonia, diphenylamidophosphate, $PO.NH_2.(OC_6H_5)_2$, a beautifully crystalline substance, is at once formed. This, on saponifying with ammonia or baryta, gives phenylamidophosphoric acid, $PO.NH_2.(OC_6H_5).(OH)$, and with caustic potash or soda, amidophosphoric acid. The free acid, obtained by decomposing the lead salt by sulphur-

[1] Ann. chim. phys. [3] **18**, 188.
[2] Ann. Chem. (Liebig) **101**, 304.
[3] Journ. Chem. Soc. [2] **7**, 18.
[4] Quar. Journ. Chem. Soc. **3**, 353; Journ. Chem. Soc. [2] **2**, 225; [2] **4**, 1, 290; [2] **6**, 64, 261; [2] **7**, 15.

etted hydrogen, and precipitating with alcohol, is a well characterised body, forming fine microscopic crystals. It forms two series of salts, acid and neutral, of which the acid salts are invariably, the neutral often, crystalline, and in many cases the forms are characteristic. Boiled in aqueous solution, either alone or with an acid, it decomposes almost instantly into ammonia and orthophosphoric acid. Its cold aqueous solution may be kept a short time without much decomposition, but quickly passes into primary ammonium orthophosphate. Dilute mineral acids in the cold effect the change much more rapidly, but in either case the first product is not orthophosphoric acid, but an acid or mixture of acids giving white amorphous precipitates with silver nitrate. At 100° the dry acid passes without loss of weight into an ammonium salt, giving a white silver salt. This is possibly metaphosphate, or a mixture of the different metaphosphates,

$$\begin{matrix} NH_2 \\ PO\ OH \\ OH \end{matrix} = PO_3(NH_4),$$

but the nature of the product has not yet been established. The acid salts on heating give off ammonia and leave metaphosphates. Such of the neutral salts as contain crystal water pass first into ammonium salts, and on further heating into pyrophosphates. The neutral silver salt, which is anhydrous, is an exception. At 180° it gives off one half its nitrogen as ammonia, apparently forming a very stable *pyrimidophosphate*,

$$NH\begin{matrix} PO(OAg)_2 \\ PO(OAg)_2 \end{matrix},$$

which stands a red heat without further change, or at least without loss of weight. Other salts which are especially characteristic are the acid sodium salt, almost insoluble in water, and the neutral magnesium salt, isomeric with crystallised ammonium magnesium phosphate. In the absence of any experimental proof of the contrary, the constitution of the acid is regarded as $PO\begin{matrix} NH_2 \\ (OH)_2 \end{matrix}$, in accordance with the usually assumed structure of acid amides, rather than $P(NH)(OH)_3$, in harmony with the most recent views on the nature of organic amides.

Descriptive Part.

Diphenylamidophosphate, $PO\begin{matrix}NH_2\\(OC_6H_5)_2\end{matrix}$.—1 mol. wt. phosphorus oxychloride and 2 mol. wts. phenol are boiled in a flask fitted with return condenser until no further evolution of hydrochloric acid occurs. The product is a mixture of $PO(OC_6H_5)_3$, $PO.Cl.(OC_6H_5)_2$, $PO.Cl_2.(OC_6H_5)$ and unchanged oxychloride. It is not necessary to isolate the diphenylphosphoric chloride. The liquid is diluted with absolute alcohol, and alcoholic ammonia is added slowly, with cooling, to alkaline reaction. The product is mixed with several volumes of water, whereby ammonium chloride dissolves and crystalline amidophosphate separates, mixed with oily phenylphosphates. This is sucked out in a funnel as far as possible, washed with water, dried on porous plates to remove the oil, again washed, dried and recrystallised two or three times from alcohol, or better, chloroform. The yield is about 35 per cent. of the theoretical.

	Calculated for $PO.NH_2.(OC_6H_5)_2$.		Found.	
P	12.46	...	12.37	...
N	5.67	5.70	5.64	5.67

Phosphorus was determined as magnesium pyrophosphate after evaporating first with alkali, then with acid; nitrogen as ammonia after evaporating with hydrochloric acid; both as ammonium chloroplatinate and by titration, after distilling.

The ether fuses at 148°, and on cooling solidifies to a crystalline mass with a surface of brilliant facets. At 180° there is a very slow evolution of ammonia and phenol, which becomes quite rapid at 230°, when it is accompanied by sublimation of unchanged substance. The non-volatile product of decomposition is first an oil, later a solid substance containing phosphorus.

Phenylamidophosphoric acid, $PO\begin{matrix}NH_2\\OC_6H_5\\OH\end{matrix}$.—The free acid could not be obtained in the solid state. On decomposing the lead salt in the cold with sulphuretted hydrogen a solution is obtained which is not precipitated by alcohol. On evaporating *in vacuo* over sulphuric acid, the acid takes up water and is converted into the acid ammonium salt of phenylphosphoric acid, which contains only traces of amido acid, which were isolated as the silver salt described below.

Acid ammonium phenylphosphate is easily soluble in water, and crystallises in long prisms. It also crystallises from alcohol, in which it is difficultly soluble, as pearly rhombic plates or flat needles, fusing at 140°–145° with decomposition. Silver nitrate gives a precipitate of radiating flat prisms consisting of the *neutral silver salt*, (*a*) which is anhydrous. By neutralising the filtrate with ammonia a further precipitate of the same salt (*b*) is obtained.

	Calculated for $PO\begin{matrix}(OAg)_2\\OC_6H_5\end{matrix}$.	Found. (*a*)	(*b*)
Ag	55·64	54·88	55·44

Phenylphosphoric acid therefore resembles phosphoric acid in that its acid salts give directly the neutral silver salt, and differs from amidophosphoric acid, which gives either acid or neutral silver salt according as acid or neutral salt be used as precipitant.

Ammonium phenylamidophosphate, $PO\begin{matrix}NH_2\\OC_6H_5,\\ONH_4\end{matrix}$ obtained by saponifying the diphenyl ether with aqueous ammonia, is easily soluble in water, and the solution may be evaporated without decomposition.

Silver phenylamidophosphate, $PO\begin{matrix}NH_2\\OC_6H_5,\\OAg\end{matrix}$ from the ammonium salt, after recrystallising from water, forms scales or long, narrow, pointed plates of pearly lustre. It is difficultly soluble in cold, moderately in boiling water, and has a strong tendency to separate as a crystalline scum on the surface. It is unaffected by light.

	Calculated for $PO(NH_2)(OC_6H_5)(OAg)$.	Found.		
P	11·09	...	11·11	...
N	5·02	...	5·08	...
Ag	38·53	38·31	...	38·19

Barium phenylamidophosphate is formed by boiling the ether with baryta water until nothing crystallises out on cooling, and removing the excess of baryta by carbon dioxide. It forms scales, is quite soluble in water, and resembles the silver salt in forming a crystalline scum on the surface.

Lead phenylamidophosphate, from the barium salt by lead acetate, forms brilliant scales, nearly insoluble in water.

Amidophosphoric acid, $PO\begin{matrix}NH_2\\(OH)_2\end{matrix}$.—The alkali salts of this acid are readily obtained by saponifying the ether with a strong solu-

tion of caustic potash or soda. The chief difficulty in obtaining them pure is in separating them from the small quantity of phosphate formed at the same time. In the case of some of the salts this may be effected by methods mentioned below. The conversion into phosphate by boiling alkali is very slow. A weighed amount of ether was boiled with concentrated caustic potash, and the ammonia determined in the distillate by titration. An hour's boiling showed a decomposition of only three per cent.

Acid potassium amidophosphate, $PO\begin{matrix}NH_2\\OK\\OH\end{matrix}$. — If a lump of caustic potash be placed on some diphenyl ether and a few drops of water be added, a somewhat violent reaction occurs. On boiling with an excess of concentrated caustic potash, the saponification is complete in ten minutes. The oily solution is acidified with strong acetic acid, care being taken to keep it cool with ice-water. On adding several volumes of alcohol, the acid salt is at once precipitated. It is purified by washing with alcohol, dissolving in a little water and reprecipitating by alcohol. It cannot be recrystallised from hot water, as its solution is rapidly converted by heating into acid potassium ammonium phosphate. A weighed amount of acid potassium salt was dissolved in water and boiled ten minutes; $\frac{1}{10}$ n. caustic soda was added in excess, and the solution again boiled to remove ammonia. The loss of alkalinity due to the escape of ammonia indicated that by ten minutes' boiling, ninety-eight per cent. of the amide was converted into ammonium salt. The same change occurs in a few days in the cold aqueous solution. The salt forms six-pointed stars, or sometimes rhombohedra, readily soluble in cold water, insoluble in alcohol. Its solution is neutral towards litmus, methyl orange and phenolphthalein. On ignition it gives off ammonia and leaves potassium metaphosphate.

The analysis of two air-dried preparations (*a* and *b*) gave—

	Calculated for $PO.NH_2.OK.OH$.	Found.		
		a.		*b*.
P	22.96	22.76		...
N	10.39	10.26	10.20	10.35

The loss on ignition gave—

	Calculated for $PO.NH_2.OK.OH$.	Found.
NH_3	12.61	13.83

The excess found is due in part to a small amount of water which the salt retains, in part to a little acid potassium ammonium phosphate which cannot be removed by precipitating with alcohol. The amount of ammonium salt may be determined by distilling off the ammonia with alkali solution, and determining it in the distillate, making a slight correction for the decomposition of the amide itself as above determined (3 per cent. per hour). In this way the amount of ammonium salt in preparation (*a*) was found to be 4.75 and 5.10 per cent., in (*b*) 4.15 per cent. As the acid potassium salt is used for preparing other salts, this small amount of phosphate has to be taken into consideration, as the latter would otherwise be contaminated with phosphate. Its presence may be obviated by methods below mentioned.

Neutral potassium amidophosphate is extremely soluble in water, and not appreciably decomposed by boiling.

Acid sodium amidophosphate, $PO\begin{matrix}NH_2\\ONa\\OH\end{matrix} + xH_2O(?)$.—This is prepared by boiling the ether ten minutes with strong caustic soda, cooling and acidifying with acetic acid. It separates at once without adding alcohol, as a crystalline powder, which is washed with dilute alcohol, dissolved in ammonia, and reprecipitated by acetic acid or carbon dioxide. It forms a heavy sandy powder consisting of well defined crystals belonging to the hexagonal system, occurring sometimes as hexagonal plates or prisms without pyramids, occasionally as very symmetrical double pyramids without prism surfaces. It is scarcely soluble in cold water, insoluble in alcohol. If boiled with water it dissolves and is at once converted into acid sodium ammonium phosphate. The same change occurs slowly at ordinary temperature under water. Like all other amidophosphates, it is instantly converted into phosphoric acid by warm dilute acids. On ignition it loses ammonia, and leaves a vitreous residue of sodium hexametaphosphate. It contains small but varying amounts of water. The analysis of one preparation gave—

	Calculated for $PO.NH_2.ONa.OH + \frac{1}{2}H_2O$.	Found.	
P	25.11	25.08	
N	11.36	11.49	11.34
Residue ($NaPO_3$)	82.54	82.43	

Other samples contained less water. This water is accounted for in part by the presence of a small amount of acid sodium ammonium phosphate, but the latter, when determined as in the acid potassium salt, was found to be only 2–2.5 per cent., while the whole amount of water present, if assumed to be in the form of ammonium salt, would make the amount 16.8 per cent. The water is therefore present mainly as such. It does not act on the amido group at 100°, as the quantity of ammonia expelled by alkali after heating at this temperature is not increased, and there is no loss of weight. At 150° it reacts, converting a portion of amide into ammonium salt, which at the same time loses ammonia, the residue being found to contain less nitrogen. The acid sodium salt dissolves rather difficultly in excess of ammonia, probably forming the sodium ammonium salt; from this solution it is reprecipitated by carbon dioxide, or even by expelling the ammonia by an air current or spontaneous evaporation. In this respect it resembles the neutral phosphates containing ammonia.

Neutral sodium amidophosphate, $PO\begin{matrix}NH_2\\(ONa)_2\end{matrix}$, is readily made by treating caustic soda solution with excess of acid salt, the excess remaining undissolved. It forms bunches of needles or prisms, extremely soluble in water, but not deliquescent. By the action of carbon dioxide, even that in the air, it is decomposed into acid salt and sodium carbonate. Alcohol precipitates it as a syrup from aqueous solution.

Acid lithium amidophosphate is precipitated by lithium chloride from a strong solution of the acid potassium salt, in the form of difficultly soluble crystalline granules. On boiling it is converted into phosphates of lithium.

Acid ammonium amidophosphate is formed by decomposing either the acid or neutral silver salt with ammonium sulphide and precipitating by alcohol. It forms a beautiful network of needles, crossing at angles of 60°, and is very soluble in water, and permanent in the air. As it is formed by precipitating an ammoniacal solution by alcohol, it appears that the neutral salt is very unstable, if capable of existence.

Potassium ammonium amidophosphate is precipitated by alcohol from an ammoniacal solution of the acid potassium salt as a syrup, which is decomposed by washing with alcohol into acid potassium salt and ammonia.

Acid hydroxylamine amidophosphate, obtained by precipitating a moderately strong solution of the acid potassium salt with hydroxylamine hydrochlorate, is difficultly soluble in water, and forms brilliant rhombic plates and prisms. Its crystallising power is greater than that of any other salt obtained. A neutral salt could not be prepared.

The preparation of salts of the earths and heavy metals from the acid potassium salt is interfered with by the latter being contaminated with a small amount of phosphate. The contamination of the precipitate in the case of the salts is best avoided by adding to the ice-cold solution of the acid potassium salt, before precipitation, a very little dilute nitric acid, which effectively holds all phosphate in solution. In making neutral salts, it is not so easy to get rid of the phosphate; the ways in which this was accomplished are given in special cases below.

Acid barium amidophosphate, $\left(PO\begin{matrix}NH_2\\OH\\O-\end{matrix}\right)_2Ba + 2\frac{1}{2}H_2O$, is obtained by adding to an ice-cold solution of acid potassium salt, faintly acidified with nitric acid, barium chloride in excess. It thus forms a supersaturated solution, which crystallises only on rubbing with a glass rod. The precipitate is washed with a little water and alcohol. It forms groups of radiating microscopic plates, and once formed is quite difficultly soluble in water. On boiling its solution, a scaly crystalline precipitate of acid barium phosphate, $BaHPO_4$, at once forms. It contains about $2\frac{1}{2}$ mols. crystal water, the greater part of which is lost at 100°, but this cannot be directly determined, owing to its tendency to pass into ammonium salt with loss of ammonia. On ignition it fuses to a glass of barium hexametaphosphate.

	Calculated for $Ba(PO_3NH_2)_2 + 2\frac{1}{2}H_2O$.	Found.
Loss ($2NH_3 + 2\frac{1}{2}H_2O$)	20.17	19.82

The residue gave—

	Calculated for $Ba(PO_3)_2$.	Found.
Ba	46.43	47.12
P	21.03	21.38

Neutral barium amidophosphate, $PO\begin{matrix}NH_2\\O\end{matrix}>Ba + H_2O$.—By mixing a dilute solution of acid potassium salt with ammoniacal

barium chloride solution, and filtering quickly from the small amorphous precipitate of barium phosphate, the salt soon crystallises. It forms very characteristic hard and brittle rhombic plates, often with truncated angles, often superposed in coincident or partly turned position, sometimes also as fine prisms with many sharply defined faces. It is unchanged at 100°, but at 150° the crystal water is taken up to form ammonium salt, which at once loses ammonia, forming acid barium phosphate, which on ignition leaves a residue of pyrophosphate, giving off but little ammonia.

	Calculated for $PO\overset{NH_2}{O}>Ba + H_2O$.	Found.
Loss of 1 mol. NH_3 at 150°	6.80	6.84
Total loss on ignition, $NH_3 + \frac{1}{2}H_2O$	10.40	10.70

The residue gave—

	Calculated for $Ba_2P_2O_7$.	Found.
Ba	61.17	61.80
P	13.84	14.44

The salt is very difficultly soluble in water. Its solution, or the liquid from which it has not yet crystallised, gives on boiling, even in the presence of an excess of ammoniacal barium chloride, a scaly precipitate of acid barium phosphate.

	Calculated for $BaHPO_4$.	Found.
Loss on ignition $\frac{1}{2}H_2O$	3.86	4.65

The residue gave—

	Calculated for $Ba_2P_2O_7$.	Found.
Ba	61.16	61.76

The salt shows a peculiar behavior when formed in the presence of strong ammonia. By mixing a solution of the acid potassium salt with strongly ammoniacal barium chloride, an amorphous precipitate is formed, which dissolves (excepting traces of phosphate) on adding water. Strong ammonia reprecipitates it, and more water dissolves it; this process may be repeated several times. The solution soon deposits crystals of the neutral salt, and the precipitate itself soon turns to scales of the same substance. Filtered off and washed with ammonia, it gave on analysis figures corresponding to those of the neutral salt.

Acid calcium amidophosphate, obtained like the barium salt, is much less soluble than the latter, and forms spherical aggregations of needles.

Neutral calcium amidophosphate is formed like the neutral barium salt, but is much less soluble. Its crystallising power is also much less. From very dilute solutions it separates gradually in the form of microscopic groups of flat-pointed prisms; from concentrated solutions as an amorphous precipitate which does not become crystalline, while from solutions of intermediate strength it is at first amorphous but gradually becomes crystalline.

Acid magnesium amidophosphate, $\left(\begin{matrix}NH_2\\POOH\\O—\end{matrix}\right)_2Mg + 3\frac{1}{2}H_2O$.—

On mixing an ice-cold strong solution of acid potassium salt, acidified slightly with nitric acid, with magnesium chloride, nothing separates, even after many hours. On rubbing with a glass rod, crystallisation starts at once. Once separated it is almost insoluble in water, and forms microscopic granules consisting of radiating needles or prisms. It is insoluble in ammonium chloride. At 100° it retains 2 mols. water; on ignition it gives off ammonia and water, and leaves magnesium metaphosphate.

	Calculated for $Mg(PO_3NH_2)_2 + 3\frac{1}{2}H_2O$.	Found.
Loss ($2NH_3 + 3\frac{1}{2}H_2O$)	33.71	33.86

The residue gave—

	Calculated for $Mg(PO_3)_2$.	Found.
Mg	13.18	12.85
P	34.10	33.88

Neutral magnesium amidophosphate, $POO\begin{matrix}NH_2\\O\end{matrix}>Mg + 7\,H_2O$.—

This salt has the same empirical composition as crystallised ammonium magnesium phosphate, $MgNH_4PO_4 + 6H_2O$, but differs entirely in its properties. It forms at once on adding magnesia mixture to a solution of acid potassium salt, or better, by precipitating neutral sodium salt with a magnesium salt. Any phosphoric acid present is first thrown down by a little of the precipitant, either as magnesium or magnesium ammonium phosphate; even when phosphoric acid is in excess it is completely thrown down by magnesia mixture before any amidophosphate forms, and the change can easily be followed by observing the crystals under the microscope. From solutions containing ammonium chloride (as when magnesia mixture is used) it crystallises

in very characteristic plates, often nearly rectangular, but more frequently with truncated angles, forming oblong octagonal plates. In the absence of ammonium salts it forms thick prisms, in either case easily distinguishable from ammonium magnesium phosphate. It is difficultly but perceptibly soluble in water, and quite readily in dilute ammonium chloride solution, and may be separated from any accompanying ammonium magnesium phosphate in this way. From its aqueous solution ammonia precipitates magnesium hydroxide. On boiling its aqueous solution, ammonium magnesium phosphate is at once formed. It dissolves in acetic acid; from its solution in nitric acid, alcohol precipitates acid salt. Even when free from ammonium salt, caustic potash causes more or less evolution of ammonia in the cold. Over sulphuric acid it quickly loses most of its crystal water, but the last two or three molecules are given off very slowly, and constant weight could not be obtained. At 100° it loses somewhat more than 5 mols., but this cannot be accurately determined, as at this temperature partial decomposition of the amide with loss of ammonia occurs, as shown by analysis of the residue. On ignition it leaves magnesium pyrophosphate.

	Calculated for $MgPO_2NH_2 + 7H_2O$	Found.	
P	12.67	12.59	
N	5.73	6.53	6.27
Mg	9.79	9.77	
Loss on ignition	54.70	54.79	

Acid manganese amidophosphate, prepared like the acid magnesium salt, forms faintly pinkish microscopic crystals, or granular and lenticular forms. It contains crystal water, is difficultly soluble, and shows no tendency to form supersaturated solutions.

Neutral manganese amidophosphate, from the neutral sodium salt, is an amorphous white precipitate.

Acid zinc amidophosphate is difficultly soluble in water; soluble in acetic acid and in ammonia. It crystallises readily in small but finely-formed rhombic prisms with pyramids, or in hexagonal plates.

Neutral zinc amidophosphate is an amorphous white precipitate, perceptibly soluble in water. Both salts are converted into phosphate by boiling.

Cobalt amidophosphates. The *acid* salt forms readily from the acid potassium salt with a cobalt salt, after adding a drop of nitric

acid. It is difficultly soluble in water; soluble in ammonia, and forms pink granules. The *neutral* salt is an amorphous pink precipitate.

Nickel amidophosphates. The *acid* salt has a great tendency to supersaturation, and can only with great difficulty be made to crystallise. Once formed, it consists of minute crystalline granules, difficultly soluble in water. The *neutral* salt is an amorphous, nearly colorless precipitate, soluble in acetic acid and in ammonia.

Ferrous amidophosphates. The *acid* salt, formed as above, crystallises very readily in nearly colorless microscopic crystals, apparently of the regular system, and consisting of the dodekahedron or combinations of cube and octahedron. It is nearly insoluble in water or ammonium chloride; soluble in ammonia. The *neutral* salt is a dirty greenish, amorphous precipitate, soluble in much water, in acetic acid and in ammonia.

Ferric amidophosphates. Both acid and neutral alkali salts give, with a neutral solution of ferric chloride, white, amorphous precipitates, soluble in excess of amidophosphate and in ammonia, insoluble in acetic acid.

Aluminium amidophosphate. Neutral sodium salt gives, with alum, a white, amorphous precipitate, completely soluble in ammonia.

Chromic amidophosphate, from neutral sodium salt, is a very nearly colorless amorphous precipitate, soluble in ammonia on warming.

Cupric amidophosphates. The *acid* salt crystallises in rosettes and dumb-bell-like forms, nearly insoluble in water. The *neutral* salt is an amorphous precipitate, slightly soluble in water, and converted into phosphate by boiling.

Mercuric amidophosphates. Neither acid nor neutral salts are precipitated by mercuric chloride. On boiling, mercuric phosphate is formed.

Cadmium amidophosphates. By mixing solutions of acid potassium amidophosphate and cadmium chloride, crystalline precipitates somewhat soluble in water are obtained. These differ in form according as one or the other reagent is in excess; with excess of cadmium chloride a double salt is formed, which gives off ammonium chloride on heating.

Lead amidophosphate. Acid potassium salt and lead acetate give a precipitate consisting of groups of radiating plates, slightly soluble in water, presumably acid salt.

Acid silver amidophosphate, $PO\begin{matrix}NH_2\\OAg\\OH\end{matrix}$.—This may be obtained by precipitating the acid potassium salt with silver nitrate, but, thus obtained, it contains too much silver (about 2 per cent.), due, perhaps, to a small amount of neutral salt or to a trace of phosphate. By previously adding a very little nitric acid to the cold solution, it is obtained pure. As it is somewhat soluble in water, the theoretical yield cannot be obtained. It is also formed by dissolving the neutral salt in cold dilute nitric acid and precipitating by alcohol, or by adding alcohol to a solution of the free acid and silver nitrate. It forms a heavy crystalline powder, consisting of short needles, or, oftener, of very thick, short, hexagonal prisms with pyramidal ends, united into groups or twins; also, by precipitating with alcohol, as hexagonal stars. The forms are very characteristic. It is difficultly but appreciably soluble in water, easily in dilute nitric or acetic acid, and in ammonia; from the latter solution it crystallises on evaporation. The aqueous solution is at once converted into phosphate by boiling. Light does not discolor it. The air-dried salt is anhydrous. Analysis gave:

	Calculated for $PO\begin{matrix}NH_2\\OAg\\OH\end{matrix}$.	Found.
P	15.22	15.23
Ag	52.90	53.35

On ignition it loses ammonia and leaves an easily fusible glass of silver hexametaphosphate.

	Calculated for $PO\begin{matrix}NH_2\\OAg\\OH\end{matrix}$.	Found.
Loss (NH_3)	8.36	8.17

Neutral silver amidophosphate, $PO\begin{matrix}NH_2\\(OAg)_2\end{matrix}$.—This is obtained either by adding silver nitrate and then ammonia to the filtrate from the acid salt, or (with much loss) by dissolving the acid salt in very dilute nitric acid, and adding silver nitrate and ammonia. It forms at first a turbidity, which in a few moments turns to a quickly subsiding crystalline precipitate. The ammonia must be added cautiously, and stopped as soon as the salt ceases to subside quickly. At this point a nearly white amorphous substance of unknown composition is formed, which remains in suspension, and may be redissolved by a drop of nitric acid. Further

addition of ammonia to the filtrate gives the same amorphous salt, which is faintly yellow, and rapidly blackens in the light. It may also be obtained from the neutral sodium salt, but this method is not to be recommended, as the product is slightly yellow. The best method is the first mentioned, and if very dilute solutions of acid potassium salt have been used, nearly all the acid silver salt remains in solution and can be converted into neutral salt as described. The neutral salt forms characteristic microscopic rhombic plates, with angles of nearly 60°, often united to bunches. It is colorless and unaffected by light. The crystalline powder is soft, and can thus be distinguished from the acid salt, which is gritty. It is almost insoluble in water; soluble in nitric acid, from which solution alcohol precipitates acid salt; soluble in ammonia, and deposited unchanged on spontaneous evaporation. The air-dried salt is anhydrous.

	Calculated for $PO.NH_2(OAg)_2$.	Found.	
P	9.98	10.03	9.87
N	4.52	4.51	
Ag	69.40	69.18	69.15

It remains unchanged at 150°; at 180° it loses weight, the loss corresponding to one-half the total nitrogen calculated as ammonia. On heating to constant weight at 180°—

	Calculated for $2PO.NH_2(OAg)_2 - NH_3$.	Found.
Loss,	2.74	2.82

The residue is brownish, but may be fused over the blast with but slight loss, whereby a little oxygen escapes, and a small amount of metallic silver is formed. In the above case this was weighed, and found to be only 5.61 per cent. out of a total of 69.40 per cent. The loss between 180° and red heat was 0.34 per cent., and this is exactly the amount of oxygen which would be given off by the silver oxide corresponding to 5.61 per cent. silver. The residue on ignition consists, besides metallic silver, of a yellow glass, soluble in ammonia. Probably there is formed at 180° the silver salt of *pyrimidophosphoric acid*,

$$NH\begin{matrix}<\\ \end{matrix}\begin{matrix}PO(OH)_2\\ PO(OH)_2\end{matrix},$$

which is not decomposed by fusion. Attempt will be made to isolate the free acid.

If the salt be heated at once over the blast, without previous heating at 180°, the decomposition is markedly different, much more metallic silver being formed.

	Calculated for ½N as NH_3.	Found.
Loss,	2.74	4.63
Free silver,	...	25.75

This amount of silver corresponds to 1.91 per cent. oxygen, which with 2.74 per cent. ammonia makes 4.65 per cent. loss, the amount actually found. The formation of silver oxide is due to the liberated ammonia, which splits off silver oxide and water, forming a higher amide. The action of dry ammonia gas on the salt is scarcely appreciable at 180°, as was found by experiment, hence the salt may be heated at this temperature without the ammonia which is given off liberating any considerable amount of silver oxide, as seen in the first case. At 200° and higher, dry ammonia forms large amounts of silver oxide and water, and therefore on heating rapidly, as in the second case, the liberated ammonia is able to act, and the large amount of silver formed is accounted for. The products of the action of dry ammonia on this salt will be described in a future article, when it will also be shown that amidophosphates may be made from neutral silver phosphate in this way. Experiments towards forming other inorganic amides by this method are also in progress.

Free Amidophosphoric Acid.

The isolation of the free acid is attended with difficulties, owing to its unstable nature. It has not yet been obtained perfectly pure, and the yield is always far below the theoretical. The silver salts may be decomposed by hydrochloric acid in the cold, and the solution precipitated by alcohol, but a deficiency of acid causes the solution to be contaminated with acid salt, and an excess destroys the amido acid completely, or at least prevents its precipitation. The decomposition of the silver salts by sulphuretted hydrogen gives better, but unsatisfactory, results. The best results are obtained by suspending the lead salt in a little ice-water, and decomposing by sulphuretted hydrogen. It is essential to have the latter in excess, as otherwise the solution contains some lead salt. The filtrate is run into four or five volumes of alcohol, whereby the acid is at once precipitated in the form of

microscopic crystals. These consist sometimes of thick plates, sometimes of forms which appear to be cubes, but which are anisotropic. It is insoluble in alcohol, easily soluble in water, the solution having a sweetish taste. It gives no precipitate with silver nitrate, unless on addition of ammonia or alcohol. It evolves no ammonia with caustic alkalies, and is easily converted into the characteristic sodium, magnesium, barium and silver salts, hence there can be no question as to its nature. It may be exposed to the air for a long time without change, but gradually alters, becoming pasty, in which condition it precipitates silver nitrate directly, and hence has become converted into an ammonium salt. The precipitate is white and amorphous, hence not phosphate. Its solution, if boiled but a moment, also gives a white silver precipitate, but, on boiling several minutes, it is completely converted into phosphate. It does not lose weight at 100°, but is slowly converted into ammonium salt, giving a white silver precipitate direct. Whether the product is one of the isomeric ammonium metaphosphates has not yet been determined. At 150° it also loses nothing, but fuses partially, and on higher heating it gives off ammonia. The silver salt from the acid which has been heated just to fusion becomes pasty under boiling water, like silver hexametaphosphate. The free acid obtained as above did not give satisfactory results on analysis, and such data are therefore postponed.

The alcoholic filtrate from the free acid contains an abundance of ammonium salts, giving amorphous, white, silver precipitates.

The action of amidophosphoric acid towards indicators is not sharp. The free acid gives acid reaction, the acid alkali salts have neutral reaction, but no sharp transitions can be obtained either with litmus, methyl orange or phenolphthalein. It also differs from phosphoric acid in the uniformity with which its acid alkali salts precipitate acid salts, and its neutral alkali salts give neutral salts. No exception to this was observed. Soluble acid phosphates, as is well known, give, with silver and many other metals, precipitates of neutral salt.

The investigation will be continued in the directions indicated. The above data were worked out, for the most part, in the chemical laboratory of the United States Geological Survey, in Washington, and I am indebted to the director, Major Powell, and to Professor F. W. Clarke, for the opportunity of so doing.

CHICAGO, *Jan.*, 1893.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

DERIVATIVES OF NITROGEN HALOGEN COMPOUNDS.

First Paper.

By Felix Lengfeld and Julius Stieglitz.

An article by Seliwanow in Berichte **25**, p. 3617, on "Mixed Anhydrides of Hypochlorous and Analogous Acids," leads us to publish this preliminary report. Our work was undertaken for the purpose of obtaining substituted hydroxylamines and hydrothiamines (NH_2SH) by the action of the compounds ROMe and RSMe on HalNR, and of ROHal and RSHal on MeNR. We propose continuing our work in this direction, and shall, of course, avoid as far as possible questions dealing with the derivation of the halogen amides and amines from hypochlorous and analogous acids, as outlined in Seliwanow's paper.

As the substituted succinimides $C_2H_4(CO)_2NR$ are readily decomposed into succinic acid and amines, it is probable that compounds $C_2H_4(CO)_2NOR$ will yield hydroxylamines without difficulty; and this, together with the fact that succinimide is easily obtained, led us to begin our investigation with the halogen derivatives of succinimide. We found that succinimidebromide (bromylsuccinimide, if Seliwanow's nomenclature is adopted) can be prepared in quantity with little trouble. This was acted on with sodium alcoholates in order to obtain oximethers of succinic acid according to the equation

$$\begin{matrix} CH_2{-}CO \\ | \\ CH_2{-}CO \end{matrix} \!\!>\!NBr + NaOR = \begin{matrix} CH_2{-}CO \\ | \\ CH_2{-}CO \end{matrix} \!\!>\!NOR + NaBr.$$

The reaction, however, is not so simple.

Succinimidebromide,

$$\begin{matrix} CH_2{-}CO \\ | \\ CH_2{-}CO \end{matrix} \!\!>\!NBr \text{ or } \begin{matrix} CH_2{-}C{-}O{-}Br \\ | \\ CH_2{-}C{-}O \end{matrix} \!\!>\!N \quad .$$

20 grams of succinimide are dissolved in a solution of 8 grams sodic hydrate in 50 cc. water, placed in cracked ice, and 32 grams bromine slowly added. The first few drops of bromine produce a white crystalline precipitate which, on further addition, increases

so that the mass becomes thick and pasty. It is rapidly filtered, washed with a little ice-water and brought on clay plates. Any excess of bromine volatilises, and a microcrystalline, almost colorless powder, sufficiently pure for most purposes, remains. The yield is from 90 to 95 per cent. of the theoretical. A slight variation in the details, such as the use of potassic instead of sodic hydrate, or the addition of the alkali to a mixture of bromine and succinimide, does not affect the result. A perfectly white compound may be obtained by replacing one-fourth of the water by ethyl alcohol. The reaction is evidently as follows:

$$C_4H_5NO_2 + NaOH + Br_2 = \begin{matrix} CH_2{-}CO \\ | \\ CH_2{-}CO \end{matrix} > NBr \text{ or}$$

$$\left(\begin{matrix} CH_2{-}C{-}O{-}Br \\ | \quad\quad > N \\ CH_2{-}C{-}O \end{matrix} \right) + NaBr + H_2O.$$

For analysis, the compound was washed repeatedly with cold water and dried first on clay plates, then in a vacuum over sulphuric acid, and finally in an air-bath at 80° for one hour. The following results were obtained:

I. 0.2285 gram substance gave 0.225 gram CO_2 and 0.0528 gram H_2O.

II. 0.2261 gram substance gave 14.7 cc. moist N at 4.5° and 747 mm.

	Calculated for $C_4H_4NO_2Br$.	Found.	
		I.	II.
C	26.97	26.84	...
H	2.25	2.57	...
N	7.87	...	7.85

Succinimidebromide melts at 172.5° when slowly heated, and at 177.5°–178.5° when rapidly heated. Pure, it melts with but slight decomposition, and recrystallises on cooling. When it contains even a trace of impurity, its fusion is attended with decomposition and evolution of gas. From hot benzene (in which it is sparingly soluble) it crystallises in short tetragonal prisms with pyramidal terminations. It has, in general, the same properties as acetbromamide.[1] Acids instantly liberate bromine, regenerating succinimide; with ammonia it gives nitrogen; with aniline it reacts with explosive violence, and with sodium phenolate it

[1] Hofmann, Ber. **15**, 411.

forms tribromphenol. Water decomposes it slowly, the solution bleaching. Pure and dry, it is stable and may be kept indefinitely. It is evidently analogous to succinimideiodide prepared by Bunge[1] by the action of iodine on silver succinimide in anhydrous solution, and to succinimidechloride obtained by Bender[2] from succinimide, bleaching powder and hydrochloric acid. It would seem, however, to be somewhat more reactive, as all attempts to replace the halogen in the chlor- and iodo-compounds have failed,[3] and the following reactions show that the bromine is replaceable.

Action of Succinimidebromide on Sodium Methylate in Dilute Solution.

The action of sodium methylate in methyl alcohol on succinimidebromide varies with the concentration. 1 gram sodium (1 atom) is dissolved in 40 grams pure methyl alcohol, the solution cooled, 8 grams succinimidebromide (1 molecule) added, and the whole boiled on a water-bath with inverted condenser forty minutes. It is now alkaline, but gives no bromine on adding hydrochloric acid. It is almost neutralised with hydrochloric acid, and then acetic acid in slight excess is added. The methyl alcohol is removed by distillation, the residue repeatedly extracted with chloroform, and the chloroform, after washing first with a very dilute sodic hydrate solution, then with acidulated and pure water, and drying, distilled off. There remains a straw-colored oil which solidifies in a freezing mixture, but melts again at the ordinary temperature of the laboratory. It is a mixture of at least two compounds, one of which is readily, the other difficultly soluble in ether. The difficultly soluble compound is present in but small quantity and is identical with the substance described on p. 219. The ethereal solution on evaporation leaves an oil which may be distilled in a vacuum. The main portion goes over between 145.5° and 146.5° (thermometer in the vapor) at 20 mm. pressure. It is a colorless oil which soon solidifies to a crystalline mass, especially on cooling or stirring. It now remains solid at the temperature of the laboratory. It melts at 33.5°, is odorless, and easily soluble in water and the organic solvents, with the exception of ligroin. The yield of crude oil is about 55 per cent. of the theoretical, of pure substance about 40 per cent. We have not yet further investigated

[1] Annalen, Sup. **2**, 119. [2] Berichte **19**, 2273.
[3] Bunge, loc. cit.; Bender, loc. cit. p. 2274; Seliwanow, loc. cit., 3620, etc.

the residue left on distilling the crude oil. The compound melting at 33.5° was powdered, put on a clay plate and left in a vacuum over sulphuric acid for forty-eight hours. Analysis then gave the following results:

I. 0.2194 gram substance gave 0.3576 gram CO_2 and 0.1354 gram H_2O.

II. 0.2058 gram substance gave 0.330 gram CO_2 and 0.1281 gram H_2O.

III. 0.2328 gram substance gave 0.3790 gram CO_2 and 0.148 gram H_2O.

IV. 0.210 gram substance gave 15.4 cc. moist nitrogen at 11° and 750.3 mm.

	Calculated for $C_6H_{11}O_4N$.	Found. I.	II.	III.	IV.
C	44.72	44.45	44.13	44.40	...
H	6.83	6.86	6.92	7.06	...
N	8.70	...	...	...	8.63

A determination of the molecular weight by the cryoscopic method, water as solvent, gave the following:

Weight of water used, 15.17 grams.

I. 0.352 gram substance depressed the melting-point 0.279°.

II. 0.643 gram substance depressed the melting-point 0.48°.

III. 0.9585 gram substance depressed the melting-point 0.69°.

Molecular weight calculated for $C_6H_{11}O_4N$.	Found. I.	II.	III.
161	158	167.8	174

We have evidently a compound of the formula $C_6H_{11}O_4N$ formed by the following reaction:

$$C_2H_4(CO)_2NBr + NaOCH_3 + HOCH_3 = C_6H_{11}NO_4 + NaBr.$$

The method of formation suggests the constitution

$$\begin{array}{l} CH_2—COOCH_3 \\ | \\ CH_2—CONH.OCH_3 \end{array}.$$

Such a substance should give substituted hydroxylamines, and like the oxime ethers $C{=}O{<}^{NHR^1}_{O_2R}$ readily yield an acid by the substitution of hydrogen for carboxylic methyl. On shaking with milk of lime,[1] the calcium salt of an acid is indeed formed. The alkaline

[1] Wallach: Annalen **184**, 58.

solution is washed with ether, and after acidifying with hydrochloric acid, repeatedly extracted with ether or chloroform. On distilling the solvent, a colorless oil which soon solidifies remains. It may be purified by dissolving in a little chloroform and precipitating with ligroin (boiling-point 40°–60°). For analysis it was prepared in this way and dried on clay plates in a vacuum over sulphuric acid for 48 hours. The following results were obtained:

I. 0.2035 gram substance gave 0.300 gram CO_2 and 0.115 gram H_2O.

II. 0.2539 gram substance gave 21.0 cc. moist nitrogen at 19.5° and 747.7 mm.

	Calculated for $C_5H_9NO_4$.	Found. I.	II.
C	40.81	40.21	...
H	6.12	6.28	...
N	9.52	...	9.54

Analysis agrees with a compound, $CH_2\!-\!\overset{\overset{O}{\|}}{\underset{|}{C}}\!-\!NHOCH_3$.—The $CH_2\!-\!COOH$.

substance has acid reaction, taste and properties. It melts at 77°–77.5° and is easily soluble in water and the organic solvents, excepting ligroin. From ether it crystallises in fan-like acicular aggregates. It will be carefully studied. From it and the substance melting at 33.5°, probably its methyl ether, we are now trying to obtain α-methylhydroxylamine.

Action of Sodiummethylate in Concentrated Solution on Succinimidebromide.

1 gram of sodium (1 atom) was dissolved in 8 grams of pure methyl alcohol, and to the cold solution 8 grams (1 molecule) succinimidebromide added. An energetic reaction immediately takes place, the mixture becoming so warm that the methyl alcohol boils. The reaction is completed by heating 10 to 15 minutes on a water-bath. After cooling the mixture, it is nearly neutralised with hydrochloric acid and then rendered slightly acid with acetic acid and evaporated. The residue is treated exactly as described above (page 217). The oil remaining after driving off the chloroform readily deposits a mass of crystals when treated, in a freezing mixture, with ether. The crystals may be

separated by filtration from the ethereal solution and dried on clay plates. A second crop of these crystals having been obtained from the mother-liquor by evaporating the solvent, cooling and adding very little ether, the ethereal washings now leave on evaporation only a small amount of an oil, which in a freezing mixture gives white crystals, melting at 33.5°, and identical with the compound $C_6H_{11}NO_4$ described above. The chief product of the reaction, already quite pure, was purified for analysis by repeatedly dissolving in very little chloroform, cooling in an ice-mixture and precipitating with ether. The compound thus obtained melts at 65.5°, is readily soluble in water, alcohol and chloroform, difficultly soluble in ether, and crystallises from ether in stellar acicular aggregates. For analysis the substance was dried at 100°.

I. 0.2346 gram gave 0.1307 gram H_2O and 0.3942 gram CO_2.
II. 0.1461 gram gave 13.7 cc. moist nitrogen at 9° and 747 mm.
III. 0.2097 gram gave 0.118 gram H_2O and 0.3513 gram CO_2.
IV. 0.229 gram gave 0.1312 gram H_2O and 0.3883 gram CO_2.
V. 0.1575 gram gave 15.1 cc. moist N at 17.5° and 751 mm.

	Calculated for $C_{10}H_{16}O_6N_2$.	Found. I.	II.	III.	IV.	V.
C	46.15	45.80	...	45.7	46.24	...
H	6.15	6.18	...	6.25	6.37	...
N	10.77	...	11.11	...	...	11.15
O	36.93	...	...	...	...	...

A cryoscopic determination of the molecular weight, using benzene as solvent, gave abnormally high values (400 and over) which varied with the concentration. With water the values proved normal.

Weight of water used, 16.87 grams.
I. 0.0903 gram substance gave a mp. depression of 0.042°.
II. 0.3488 gram gave 0.1475°.
III. 0.5768 gram gave 0.2465°.

Calculated for $C_5H_7NO_2$.	Calculated for $C_{10}H_{16}O_6N_2$.	Found. I.	II.	III.
129	260	242.1	266.3	263.5

The average yield obtained from 40 grams succinimidebromide was 30 grams crude $C_{10}H_{16}O_6N_2$ and only very little $C_6H_{11}NO_4$. The result of the reaction is therefore, in so far as the relative quantities of the products are concerned, the reverse of that when working with dilute solution. In working in concentrated solu-

tion, *succinimide* is always formed; being difficultly soluble in chloroform, it crystallises first, when the chloroform extraction of the reaction residue has not been washed with dilute sodic hydrate. The succinimide was identified by its melting-point (124°) and its general behavior. It is no doubt formed by the reducing action of the methyl alcohol on the imidebromide, the odor of formaldehyde being quite noticeable during the reaction. It is very probable that the formation of the compound $C_{10}H_{16}N_2O_6$ depends on this previous formation of succinimide, according to the following equation:

$$C_2H_4C_2O_2NBr + C_2H_4C_2O_2NaN + 2CH_3OH = NaBr + C_{10}H_{16}O_6N_2.$$

If this view is correct, the principal reaction is essentially of the same nature in dilute and in concentrated solution,—succinimidebromide reacting in the first case with *sodium methylate* and methyl alcohol, in the second case with *sodium succinimide* and methyl alcohol. The decomposition of $C_{10}H_{16}N_2O_6$ tends to confirm this view. On being treated with concentrated hydrochloric acid in the cold (2 days) or at 100° (at once), it yields about equal quantities of *succinic acid* (identified by its melting-point, 180°, and by qualitative tests) and of a new compound, $C_4H_6O_2N_2$. This substance is very difficultly soluble in hot absolute alcohol, and so its separation from the succinic acid, which is fairly soluble, can be readily effected. The compound was recrystallised from boiling 50 per cent. alcohol, being deposited, on cooling, in small, colorless, irregular plates. Analyses of the compound as dried at 100° gave:

I. 0.2272 gram substance gave 46.15 cc. moist N at 4.5° and 744 mm.

II. 0.232 gram gave 0.1147 gram H_2O and 0.3602 gram CO_2.

	Calculated for $C_4H_6O_2N_2$.	Found. I.	Found. II.
C	42.10	...	42.34
H	5.26	...	5.49
N	24.56	24.42	...
O	28.08	...	...

A determination of the molecular weight was made by the ebulliscopic method, the substance being but slightly soluble in cold water.

0.4813 gram substance dissolved in 23 grams H_2O raised the boiling-point 0.094°.

Calculated for $C_4H_6O_2N_2$.	Found.
114	115.7

The substance melts with some decomposition at 272°, is somewhat soluble in cold water, more readily in hot water, very little in strong alcohol, and scarcely in chloroform, ether, etc. It has a neutral reaction, and is remarkably stable, remaining unchanged when heated with conc. hydrochloric acid to 150° in a sealed tube. It is obtained from $C_{10}H_{16}N_2O_6$ by a second simple reaction, *viz.* by boiling with 1 molecule of sodium methylate in methyl alcohol. On cooling, the substance $C_4H_6N_2O_2$ crystallises out, and the filtrate yields an oil having the odor of methyl succinate.

The decomposition of $C_{10}H_{16}N_2O_6$ by hydrochloric acid may be expressed in:

$$C_{10}H_{16}N_2O_6 + 2H_2O = C_4H_6O_2N_2 + C_2H_4(COOH)_2 + 2CH_3OH.$$

The formation of $C_{10}H_{16}N_2O_6$ from two molecules of a *mononitrogen* derivative of succinic acid, and its decomposition into succinic acid and a *dinitrogen* compound, $C_4H_6O_2N_2$, indicate that the two residues in the larger molecule are linked together by one or both the nitrogen atoms and that we therefore very probably have derivatives of hydroxylamine or of hydrazine.

Further investigations are being made to prove the absolute constitution of all of these compounds, and we hope that the reactions indicated in the opening paragraph may be left to us for full investigation.

CHICAGO, *February* 7, 1893.

NOTES.

Obituary.

Frederick Augustus Genth, for many years Professor of Chemistry and Mineralogy in the University of Pennsylvania, died in Philadelphia, February 2, 1893, in the seventy-third year of his age.

He was a native of Hesse-Cassel. After studying at Heidelberg and in Liebig's laboratory at Giessen, he received his

doctor's degree at Marburg. Here, too, he served as assistant to Professor Bunsen until he came to the United States.

Professor Genth is chiefly known as a mineralogist, his work, so far as published, having been, with a few important exceptions, confined to that branch of natural science. As official mineralogist he contributed several important monographs upon the mineralogy of Pennsylvania, North Carolina, etc. His principal work on purely chemical lines was the discovery and investigation of the cobalt-ammonium compounds.

He was an exceedingly active, enthusiastic investigator from his student-days to within a short time of his death. His zeal in the encouragement of scientific research entitles him to the grateful remembrance of American mineralogists and chemists.

W. W. R.

The Electrolytic Dissociation of Acids in Solution.

In a paper entitled "Ueber die Messung kleiner Dissociationsgrade," J. E. Trevor[1] gives the results of his studies of the inverting action of weak acids and acid salts on sugar solutions at 100°. The method gave accurate results, a preliminary experiment having shown that if no hydrogen ions be present, a sugar solution may be kept 80 minutes at 100° without being perceptibly inverted. To obtain comparable results it was found necessary always to use solutions of the same strength, as the sugar concentration has an effect as yet unexplained on the dissociation.

The inverting velocity of a given concentration of hydrogen ions is more than 400 times as great at 100° as at 25°. If $c =$ the inversion-velocity of any acid, we shall have for its temperature-coefficient $I = \delta \log c / \delta T$. The author found that the values for I were practically identical for a large series of acids, including those of all possible types. As he had already shown that for dilutions greater than 200, hydrochloric acid may be considered as completely dissociated both at 25° and at 100°, it follows that, if $I =$ a constant, the dissociation of the other acids must be the same at 25° as at 100°; in other words, that the dissociation is a function of the volume only and not of the temperature. If this be true, the increase of the conductivity with the temperature is not to be accounted for by an increase in the dissociation, and the conclusions of Arrhenius[2] refer to some other property of electrolytes. In the equation of van't Hoff, $\delta \log c / \delta T = q / R T^2$, if $\delta \log c / \delta T = 0$, then $q = 0$, and what is known as the electrolytic heat of dissociation is due to another cause.

The measurements on the hydrogen dissociation of acid salts is interesting as being the first contribution to our knowledge of this subject, and it is astonishing with what accuracy these slight dissociations can be determined by this method. Of the acid sodium

[1] Ztsch. phys. Chem. **10**, 231. [2] *Ibid.* **4**, 96.

salts of the dibasic organic acids the fumarate is the only one where the hydrogen ion is 1 per cent. dissociated at a dilution of 100 : 1. From the measurements no satisfactory conclusions in regard to chemical constitution could be drawn, and the predictions of Ostwald[1] cannot be said to have been entirely confirmed.

W. D. B.

Errata.

Page 22, line 4 (from top), for "stereo-isomeric" read *identical.*

Page 22, line 22 (from bottom), for "*d.* gluconic acid" read *d. gulonic acid.*

Page 26, line 7 (from top), for "potassium" read *potash.*

Page 28, line 22 (from top), for "when several cc. were used" read *within a few cc. of the distillate.*

Page 28, line 3 (from bottom), for "40 cc. of the clear solution (see above) were treated successively with lead acetate and with sodium sulphate, and after being subjected to the process of inversion and neutralised, were filled up to 50 cc." read 40 *cc. of the clear solution (see above) which had been previously treated successively with lead vinegar and with sodium sulphate, were subjected to the process of inversion, neutralised and filled up to* 50 *cc.*

Page 30, line 27 (from top), for "of the furfurol" read "*of furfurol.*"

Page 30, line 9 (from bottom), for "0.45" read 0.045.

Page 30, line 8 (from bottom), for "0.45" read 0.045.

Page 37, line 15 (from top), for "pentoses" read *hexoses.*

[1] Ber. d. k. sächs. Ges. der Wiss., 1891, p. 233; Ztsch. phys. Chem. **9**, 553.